VOL. VI 1904

TRANSACTIONS

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

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VOLUME VI

SIXTH GENERAL MEETING

ST. LOUIS, MO., SEPTEMBER 13, 15, 16, 1904

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

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VOLUME VI 1904

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE SIXTH GENERAL MEETING OF THE SOCIETY, HELD AT ST. LOUIS, MO., SEPTEMBER 16, 1904.

(Number of members registered, 41; guests, 21; total, 69.)

The meeting was called to order at 9.45 A. M., in the Coliseum Building, St. Louis, by President Carhart, who spoke as follows:

"This is to be a joint meeting with the Bunsen Gesellschaft, of Germany, and the Faraday Society, of England. We congratulate ourselves upon having present as a delegate from the Bunsen Gesellschaft, Dr. Hans Goldschmidt. Dr. J. W. Richards has been appointed delegate of the Faraday Society from England."

President Carhart then called upon Dr. Goldschmidt to speak. Dr. Goldschmidt read the following address:

"As the delegate of the Deutsche Bunsen Gesellschaft, I have the honor to extend the best wishes to the two sister societies—the American Electrochemical Society and the Faraday Society—for the success of this joint meeting.

"In his address at the last general meeting of the Bunsen Society, in Bonn, Mr. Kershaw, of the Faraday Society, remarked that the Faraday Society and the Bunsen Society are connected by a

community of interests and aims. This is perfectly true, yet I would like to emphasize one single point. It is one link that connects the two societies most intimately, that is, their names.

"Both societies choose their names from one of the most distinguished scientists of the last century, to erect for him a monument "aere perennius," and to indicate at the same time that the members of the societies intend to follow the paths along which these two heroes of science led them. It is a very specific principle which is characteristic for both Faraday and Bunsen in their work in natural science.

"These two men, who so thoroughly knew how to extricate from Nature its most intimate secrets—how to ascertain its laws—these two men followed the same firmly pronounced principle—to recognize nothing but facts established by experiments. They were extremely cautious to keep away from any theories if they had not been proven with absolute certainty—to keep away from speculations and to recognize only the results of experiments logically designed and carefully carried out.

"Faraday, while deeply religious and even inclined towards mysticism, was most incredulous with respect to experiments—especially if somebody else had made them.

"As a student, I once proposed to my beloved master, Bunsen, a simplified analytical method by which I had three times obtained the same result. I considered this to be a sufficient proof of the reliability of the method. But Bunsen pointed out to me various difficulties and contingencies, and suggested I might come back to him with my simplified method when it would have given me exact results in 50 cases under most careful observation of all details. As a matter of fact, when tested that way, my method did not prove reliable. But it was an excellent lesson to me.

"If we endeavor to become true disciples of Faraday and Bunsen, we have to do like they did; we have to place the experiment before and above everything else; we have to draw cautiously our conclusions from the experimental facts without straying from the right way, misguided by premature hypotheses, which so often have done damage to earnest research work.

"By emphasizing these, our endeavors, which are essentially sober and practical, I hope they will find friendly recognition here, in the country of practice and industrial developments. Too often

are Americans inclined to see in European, and especially in German scientists, only poets and philosophers, leaning towards speculation, which keeps them away from practice.

"The names of Faraday and the Deutsche Bunsen Gesellschaft should be taken as a motto, indicating clearly the spirit which animates their members. It is this same spirit which connects us with the American Electrochemical Society, with its achievements and its sentiments, looking for work and development on a large industrial scale.

"I extend to you the best wishes for the success of the joint meeting of the three societies."

President Carhart: "I am sure the American Electrochemical Society is delighted to hear these cordial words from the representative of the Deutsche Bunsen Gesellschaft. We have had the good fortune to have with us once before a member of the Bunsen Gesellschaft, Dr. Haber, and now we have Dr. Goldschmidt, and we hope later, at other meetings, we shall have other representatives from our German friends. We are always glad to see them. Many of us have studied in Germany and spent a good deal of time there and have a good many friends in that country, and we are always delighted to see them. I hope the bonds between this younger Society and the Deutsche Gesellschaft will be strengthened during the years to come, and that we will have many joint meetings and much friendly intercourse. (Applause).

"Possibly Dr. Richards has been commissioned from the Faraday Society to extend some words of greeting at this time."

Dr. Richards spoke as follows: "Mr. Chairman, I had expected that some other member of the Faraday Society would be present to bring to you from abroad the greetings of our Sister Society, but since that Society has been kind enough to appoint me as one of its delegates to this joint meeting, I will take the liberty and at the same time the pleasure of extending to the American Electrochemical Society the friendly greetings of the Faraday Society, of Great Britain, and well wishes for its continued success and usefulness. The great stimulus which the formation of your American Society has had upon the growth and extension of electrochemistry in America is a cause for sincere congratulation; but the stimulus has not been confined to America alone, for wavering resolutions in England were strengthened by the story of your

success, and thus the recent development of interest in electrochemistry in Great Britain may be considered as a reflex of your activity in America. We therefore join with pleasure in joint meeting with our American co-workers in this most fascinating field of scientific and industrial activity."

President Carhart: "The American Electrochemical Society is always interested in the youngest member of the family of electrochemical societies, and I think the Faraday Society is younger than this Society by a few months. We are interested in the success of this Society in England; many of us take great pleasure in going to England from time to time, and hope to have an opportunity of attending the meetings of the Faraday Society in the future.

"About two weeks ago, I got a letter from Mr. Cowper-Coles, in which he said he regretted very much his inability to come and bring his paper listed for this occasion, but circumstances over which he had no control would necessitate his remaining in England."

Prof. Burgess moved that a vote of thanks be extended to the Organization Committee of the Fifth International Electrical Congress, for the facilities offered for the meetings. The motion was duly seconded and carried.

It was announced by the Secretary, S. S. Sadtler, that the Society had been invited to hold its annual meeting in Boston and Cambridge, Mass., by both the Massachusetts Institute of Technology and Harvard University.

The following papers were read and discussed, as printed in full in the Transactions:

H. E. Patten, "An Analytical Study of Aluminum as Deposited from Ethyl Bromide Solution."

W. D. Bancroft, "The Aluminum Rectifier."

W. McA. Johnson, "Industrial Electrochemistry."

F. A. J. Fitzgerald, "A Study of the Use of Carbon for Determining Temperatures in the Electric Furnace" (read by Prof. Richards).

W. D. Bancroft, "The Electrolytic Separation of Nickel and Cobalt."

SESSION OF SEPTEMBER 13TH.

(Held jointly with the Fifth International Electrical Congress).

Papers by the following authors were read and discussed as printed in full in these Transactions:

T. W. Richards, of Cambridge, read by G. W. Patterson (read on September 12th); J. Sigfrid Edstrom, of Christiania, Sweden; W. D. Bancroft; F. Haber and L. Bruner, of Karlsruhe, Germany, read by C. F. Burgess; L. Kahlenberg; A. G. Betts and E. F. Kern; James Swinburne, read by S. S. Sadtler; Hans Goldschmidt, of Essen-Ruhr, Germany.

SESSION OF SEPTEMBER 15TH (WITH CONGRESS).

The following papers were read and discussed, as printed in full in these Transactions:

Karl E. Guthe; Henry S. Carhart and G. A. Hulett; P. L. T. Heroult, of Le Praz, France; A. E. Kennelly and S. E. Whiting, of Harvard University; J. W. Richards; R. Lorenz, of Zurich, Switzerland, read by E. F. Roeber; Wilhelm Ostwald, of the University of Leipzig, Germany, read by W. D. Bancroft.

PROCEEDINGS OF DIRECTORS

ABSTRACTS FROM THE MINUTES OF THE MEETINGS OF DIRECTORS, HELD APRIL 7TH TO SEPTEMBER 16TH, 1904.

The following resolutions, with reference to the duties of the Secretary and Treasurer, were adopted:

Resolved, That the system of keeping the accounts of the Society, recommended by the Treasurer at the last annual meeting, be adopted.

Resolved, That in accordance with the same, all funds shall be received and receipted for and deposited by the Secretary in the name of the Society, in such depository as the Board may designate.

Resolved, That the Secretary shall obtain from the Treasurer a receipt in regular form for all moneys so deposited, which

receipt shall be issued by the Treasurer on presentation of the deposit-book, showing amount so deposited.

Resolved, That all disbursements from the Treasury shall be made upon warrants drawn upon the Treasurer by the Secretary and countersigned by the presiding officer, after approval by the Board of Directors.

Resolved, That all checks in payment of warrants shall be drawn and signed by the Secretary and countersigned by the Treasurer.

Resolved, That the Treasurer is authorized and directed to transfer all books of account to the Secretary.

It was decided that a monthly bulletin be sent out by the Secretary, this to include names of applicants to be voted upon at the next Board meeting and those elected at the one preceding, and as far as possible all notices that should be sent out for the current month.

Drs. Kahlenberg, Carhart and Bancroft were elected to represent the Society at the International Electrical Congress at St. Louis, and Prof. Burgess to serve as alternate.

It was resolved that the Society purchase a bond for $1,000, of such a character as trust companies are legally limited to purchase for trust estates.

The Secretary and Treasurer reported that in accordance with a resolution of the Board of June 3d, they had purchased a "Sewer and Construction Bond" of Lower Merion Township, Pa., No. 28, bearing 3½ per cent. interest, at par, and that the same had been placed in the hands of the Secretary for keeping. It was moved and carried that this action of the Secretary and Treasurer be accepted.

The Secretary reported that the Society had been invited both by representatives of Harvard University and the Massachusetts Institute of Technology, to meet in Boston for the spring meeting some time during April, 1905. It was at once agreed to accept the invitations and hold the spring meeting in Boston.

MEMBERS ELECTED JUNE TO OCTOBER, 1904.

June 3d.

George Breed, Philadelphia, Pa.; Alexander Lodyguine, Staten Island, N. Y.; Charles Jackson, Guadalajara, Mexico.

July 1st.

H. E. Eggers, Santa Cruz, Cal.; George G. Hitchock, Claremont, Cal.; F. L. O. Wadsworth, Morgantown, W. Va.; William C. L. Eglin, Philadelphia, Pa.; E. Humblot, San Francisco, Cal.; P. McN. Bennie, Niagara Falls, N. Y.; J. W. Best, Denver, Colo.

August 5th.

Joseph Clark, Jr., Stanley, Idaho; Benito Herrera, Los Angeles, Cal.

September 2d.

F. E. Schmitt, New York,; James G. Marshall, Niagara Falls, N. Y.; Timothy C. Root, Buffalo, N. Y.

October 1st.

Elliott M. Sergeant, Boonton, N. J.; Dr. E. P. Schoch, Austin, Tex.; Martin L. Griffin, Mechanicsville, N. Y.; Ernest S. Wittnebel, New York; F. F. Schuetz, New York.

A paper read at the Sixth General Meeting of the American Electrochemical Society, held at St. Louis, Mo., September 15, 1904.

AN ANALYTICAL STUDY ON THE DEPOSITION OF ALUMINUM FROM ETHYL BROMIDE SOLUTION.

By Harrison Eastman Patten.

In 1902, W. A. Plotnikoff[1] made the interesting discovery that aluminum bromide dissolved in ethyl bromide yields a solution of good electrical conductivity, and from this he deposited metallic aluminum. Further study of the conditions requisite for this deposition is herewith presented to the society.

It was found that even moderately high current density fails to deposit aluminum on a platinum cathode from a solution containing 4.38 per cent. of aluminum bromide by weight. The current e. m. f. curves and the discharge potentials indicate that a film is formed at the cathode. To ascertain whether this film could be removed an aluminum plate was used as cathode with a platinum anode in this 4.38 per cent. solution, and, after passing a current of near 0.5 ampère per square centimeter of cathode surface for a short time the discharge for the total cell was found to be 2.235 volts. Before being subjected to this electrolysis, the aluminum plate gave 0.632 volt against platinum in this solution. The existence of a film upon the aluminum, and the possibility of removing it are thus rendered probable, and, when taken together with other experimental checks, hardly to be questioned. A more concentrated solution containing 40.95 per cent. $AlBr_3$ in ethyl bromide was subjected to electrolysis in a dry cell between polished platinum electrodes. The solution was connected through glass U-tubes containing ignited asbestos wick, first to a second vessel containing another portion of this same solution, then to a third vessel filled with $AlBr_3$ in absolute ethyl alcohol, and finally to an Ostwald normal electrode. Current e. m. f. curves were accurately taken[2] for anode, cathode and total cell, as well as discharge poten-

[1] Jour. Russ. Phys. Chem. Soc. (3) 466, (1902).

[2] For the method, see a former paper. Decomposition Curves of Lithium Chloride in Various Alcohols, etc. Patten and Mott, Jour. Phys. Chem. 8, 153 (1904).

tials. Aluminum was deposited in crystalline form at a current density of 0.0023 ampère per square centimeter of cathode surface at 20° C. The total polarization of the cell near this current density is 2.30(±.02) volts; the anode polarization is —1.20(±.02) volts; and the cathode, +1.10(=.02) volts. By quickly shifting the electrodes from the solution to 95 per cent. ethyl alcohol scales of aluminum were removed from the cathode. The metal is coated with a film and dull. It does not adhere to the platinum but strips readily—other cathodes have not been tried as yet. Aqueous hydrochloric acid acts upon the metal evolving hydrogen. The metal reacts vigorously upon the solution from which it was deposited, giving off gases, probably largely C_4H_{10}. On the other hand aluminum which has stood in the air and acquired a protective coating has no such action on the solution, either as indicated by gas evolution or by its potential against the solution. At the anode bromine is liberated and diffuses rapidly thus rendering difficult the deposition of aluminum in quantity without the aid of a diaphragm. The process does not promise practical efficiency for the commercial deposition of aluminum.

The principal points presented are:

1. It has been shown that Plotnikoff's values for the conductivity of aluminum bromide dissolved in ethyl bromide are reliable, and his deposition of crystalline aluminum from such a solution has been confirmed.

2. Crystals of aluminum bromide near 0.5 cm. on edge were formed from the fused salt. They belong to the rhombohedral division of the hexagonal stystem, and resemble calcite. The purified aluminum bromide is not white, but a very light yellow.

3. Decomposition curves for dilute and concentrated solutions of aluminum bromide in ethyl bromide have been determined, with platinized and with polished platinum electrodes, as well as with aluminum electrodes.

4. Aluminum has a single potential of +1.10(±.02) volt, against a 40.95 per cent. solution (by weight) of aluminum bromide in ethyl bromide; and bromine, a single potential of —1.20(±.02) volt. There values neglect the possible small e. m. f. at the contact of the solutions.

5. A current density of 0.0023 ampère per square centimeter,

or about 2 ampères per square foot is just sufficient to compensate for the solvent action of the solution upon the deposited aluminum in a concentrated solution (40.95 per cent.). A dilute solution (4.38 per cent.) failed to yield aluminum even at moderately high current density.

6. An aluminum anode, which had been stripped of its film electrolytically, gave 2.235 volts in a 4.38 per cent. solution of $AlBr_3$ in ethyl bromide against a platinum cathode. Similarly magnesium gave 2.227 volts, from which, by subtracting —1.20 for bromine, we get +1.08 volt as the approximate single potential of magnesium against this solution.

7. A striking exception to the Nernst-Thompson rule is cited, in that ethyl bromide with a dielectric constant of 8.9 yields a solution of good conductivity with aluminum bromide as solute.

8. This work has a bearing upon the phenomena of the aluminum anode. A film appears to be formed upon aluminum in a solution very free from oxygen; it can be removed by using the aluminum as cathode; but the high counter pressure mentioned by Isenberg[1] and investigated by Burgess[2] and Hambuechen,[6] Zimmermann,[3] Mott,[4] and later by Cook,[5] has not been found thus far.

9. Aluminum bromide dissolved in ethyl bromide lacks the requirements of a commercial plating solution for the deposition of aluminum.

Laboratory of Physical Chemistry,
University of Wisconsin.

DISCUSSION.

PROF. BANCROFT: I understand Mr. Patten to say that the accuracy of the Ostwald zero was proved by the fact that the sum of the single potentials as measured equaled the total of the polarization. That is a mistake, I think, because the position of the zero

[1] Zeit. f. Electrochemie, 9, 278-280 (1903).

[2] Trans. Am. Electrochem. Soc., 1, 147 (1902).

[3] Thesis University of Wisconsin, 1903, under C. F. Burgess. Also Trans. Am. Electrochem. Soc., 5, 147 (1904).

[4] Electrochemical Industry, 2, 4, 129 (1904); 2, 7, 268 (1904).

[5] Physical Review, 18, 23 (1904).

[6] The Physical Characteristics of Metal Deposits, Electrochem. Ind., 1.6 (204) 1903. See also F. Fischer, Zeit. f. Physik. Chem., 48, 177 (1904).

is a purely arbitrary one. If Mr. Patten will take the value of the calomel electrode as ten volts and make his calculations on this basis, he will find that they check just as well as if he took 0.56 volts.

PROF. RICHARDS: Some years ago the thought occurred to me, and found its way into my notes, to try to obtain aluminium electrolytically from a non-oxygen containing electrolyte, using an organic liquid as the solvent for an anhydrous halogen salt of aluminium. I was unable to find the suitable solvent; and this communication comes to me, therefore, with added interest because of the success of a fellow-electrochemist in a matter in which I had been forced to confess failure.

PROF. PATTEN: Mr. Bancroft made precisely the point I myself wished to make; the actual value, 0.56 volt, was of itself immaterial, but that we are able by putting it first on one side and then the other to get the value of the voltage which was added to it.

A paper read at the Sixth General Meeting of the American Electrochemical Society, held at St. Louis, Mo., September 15, 1904.

THE ALUMINUM RECTIFIER.

By Wilder D. Bancroft.

Since a rise of temperature is recognized as being fatal to the working of the aluminum rectifier, it seemed worth while to make some runs with water-cooled electrodes. These experiments have been made by Mr. Charters, who will report on them in detail elsewhere.

The Pittsburg Reduction Co. supplied us with small aluminum tubes 2 feet long and 3/8 inch in diameter. In the preliminary experiments each tube was coiled by hand into two complete turns with the two ends extending upward. In this way a much larger surface of aluminum was exposed to the electrolyte than would otherwise have been possible. By running cold water through the tubes the temperature of the anodes could be kept down.

The first experiments were made with an aluminum anode and a platinum cathode on a direct-current circuit. The object of this was to determine approximately the point at which the electrode breaks down and also the value of the leakage current. The impressed voltage was increased gradually and the current readings were made after the values had become fairly constant. With disodium phosphate as electrolyte the leakage current was only a few hundredths of an ampère at 200 volts, and the film went to pieces at about 300 volts. With sulphuric acid, sp. gr. 1.2, the film ruptures below 100 volts. With a solution containing 67 g. crystallized citric acid per liter, the film broke at about 400 volts. When this citric acid solution was diluted to one-tenth the leakage current was only 0.3 ampères at 500 volts, and the film showed no signs of breaking down.

Citric acid solutions are of no value for a rectifier because the conductivity is too low. It is also a question whether any organic acid would withstand oxidation for any length of time. Sulphuric acid is out of the question, because it attacks the film too readily. This left disodium phosphate or phosphoric acid solutions as the

only ones available. Sodium phosphate was rejected because of the possible disadvantage of a formation of caustic soda at the aluminum electrode. The efficiency tests were therefore made with a 45 per cent. phosphoric acid solution.

The rectifier consisted of four cells so arranged as to secure all the current. Each cell contained one aluminum electrode and one lead electrode. The cells themselves were made of beakers, as these were convenient in form and size and well adapted to the purpose.

The aluminum electrodes each consisted of a piece of aluminum tubing about 9 inches long and ⅜ inch in diameter, bent into the form of a U, so that they could be placed inside of the beakers. The length of tube in the electrolyte was the same in all cases, approximately 6⅜ inches, and the area of aluminum exposed to the electrolyte was, therefore, 2.82 square inches per cell. It is very necessary that the aluminum should have very nearly the same area exposed to the electrolyte in each cell, as otherwise there would be a greater leakage than there is when the cells are evenly balanced. Care must be taken as before to avoid cutting or marring the surface of the tube, owing to the difficulty of forming a film over a roughened spot.

The two electrodes should be placed as close together as possible without forming short circuits, in order to reduce the resistance of the cell to as low a figure as possible, because such resistance in the cell cuts down the available voltage very seriously on heavy loads. In these cells the electrodes were approximately ⅜ inch apart at the bottom, and ½ inch at the top.

The aluminum electrodes were connected by rubber tubing so that cooling water could flow in at one end of the system and out at the other, keeping the tubes and electrolyte cool. The temperature was measured by two thermometers, one in the cell through which the water entered, and the other in the cell at which it left. Under ordinary circumstances these read the same, and only one reading was recorded.

The alternating current from the mains, 60 cycles and 110 volts, was led through an ammeter and a wattmeter to the rectifier. Here each side of the circuit was divided into two branches, one of which went to an aluminum electrode, and the other to a lead electrode. On the other side two aluminum electrodes were con-

nected together to form one side of the direct current circuit, and two lead electrodes were joined to form the other side. The current, after passing through the ammeter, was led to the load. It was regulated by the amount of resistance in the direct current side. When this was on open circuit, only the leakage current flowed, and under these circumstances it was comparatively small. Unfortunately, this leakage current increased with the load, though not in direct proportion to the current flowing. With no load, this leakage current amounted to between 0.3 and 0.5 ampères.

A voltmeter placed across the mains measured the pressure of the incoming alternating current. It was arranged with a double-throw switch, so that the drop in voltage across a cell could be obtained and the resistance of the cell thus determined.

Two ammeters were used on the alternating current side, one in reading from 0.0 to 2.0 ampères. These were accurately calibrated with the Thomson balance in the laboratory. The direct current ammeter was supplied with a shunt, so that it read from 0 to 10 ampères. This was also calibrated on the Thomson balance.

The A. C. voltmeter read to 130 volts, and the D. C. to 150 volts on two scales. These were carefully calibrated by a Weston voltmeter reading to 0.05 volts, belonging to the Department of Physics. The wattmeter was calibrated by means of the ammeter and voltmeter, incandescent lamps being used as a load.

It is claimed that a direct current wattmeter should be used in the direct current side, as, owing to the distorted wave form, the ammeter readings are likely to be in error. Unfortunately, one of these was not available for the test. The ammeter can, however, be checked by inserting a copper voltameter in series with it. This was done here, and the ammeter was found to be approximately correct. In case the needle was swinging at the time when a reading was to be taken, the limits of the swing were observed and the average taken as expressing as nearly as might be the correct reading.

Each cell when assembled was "formed" by applying a direct current to it, with the aluminum as the anode. The pressure was run up in one or two steps to a pressure corresponding to the alternating current pressure which the cell was to rectify. Had

an "auto" transformer been available, the aluminum could have been "formed" direct by applying a low value of alternating pressure at first, and gradually raising it to the working pressure. The aluminum having been formed and the cells arranged and all connections made, the current was turned on and a run started.

The current flowing through the rectifier was small at first and was increased step by step until the capacity of the cell was reached. During the run, readings of all the electrical instruments, as well as the temperature of the electrolyte near the aluminum tubes, were taken simultaneously every five minutes.

Each value of current was maintained for half an hour by adjusting the resistance in the direct current circuit. After changing to the next succeeding value of current, some time was allowed to pass before readings were taken in order to permit everything to settle to a state of equilibrium under the new conditions.

Each run was once repeated under exactly similar conditions, as a check on the results. The second run was usually made with a fewer number of current values to cover the range, as it was made merely as a check to the first, and the form of the curves was sure to be closely the same.

When the rectifier was in operation, gas was given off continuously in quantities sufficient to make the electrolyte almost opaque. A little water was added every day or two to compensate for that lost as gas. Otherwise the electrolyte remained unchanged, as there was no perceptible electrolytic action on the phosphoric acid. The quantity of gas given off appeared to vary directly as the current, though no quantitative measurements were made.

The current taken by the rectifier was not very steady, partly owing to the variations in voltage and to changes in the cell. At times the current would run up to half again its steady value, when there would be a sharp crackling in the cell, and the current would then subside. This action occurred especially toward the end of a run when the cell was carrying a comparatively heavy current, and was sometimes so frequent as to render it very difficult to get satisfactory electrical readings.

After the end of a run, if the circuit was opened suddenly or the load removed so that the cell was relieved at once, a sharp

crackling could be heard in the cells for a moment after the current had ceased. These crackling noises are probably due to some molecular change going on in the aluminum or in the electrolyte, or both, as the tension under which they had been working was suddenly removed.

It was found advisable to remove the aluminum tubes from the electrolyte when not in use, for there seemed to be some dissolving action in the cell, or at the surface line of the electrolyte, so that the aluminum drew an excess of current for a few moments after the circuit was closed, unless this was done. This trouble can be obviated by starting through a resistance. A small inductive resistance in the A. C. side answers quite well, as it has to carry a current for a short time only. This is advisable even when the tubes are removed from the electrolyte. In case the tubes are left in, it sometimes requires quite a little time for the excess current to subside.

The current drawn is not at unity power factor, but leads considerably. Thus the wattmeter reading is always less than the product of the volts and ampères. As the output, however, is in direct current, this power factor is not of so much importance. The power factor varies directly as the current, and approaches unity as the current approaches the capacity of the cell.

The direct current voltage obtained when the direct current end was on open circuit was much higher than when any load, however small, was put on the rectifier. A short table of results shows this clearly.

A.C. Voltmeter	A.C. Ammeter	A.C. Wattmeter	D.C. Volts
103.0	0.50	30	70
107.5	0.44	20	76
106.0	0.32	10	74
106.5	0.36	15	73
110.0	0.30	10	73

The highest voltage obtained under load seldom exceeded 50 volts, the applied pressure being the same.

Computation of Results.

The results were computed from the readings taken, in the manner shown below. The electrical quantities observed were alternating current ampères, volts, watts and direct current volts.

and ampères. The direct current ampères were obtained as the product of the direct current volts and ampères. The power factor was obtained from the alternating current values by substituting in the equation

$$ECP_f = W$$
$$P_f = W/(EC).$$

in which E = voltage, C = current, P = power factor, and W = watts.

The current efficiency was obtained by dividing the direct current output by the alternating current input, and the same applies to energy efficiency as well.

The voltage efficiency was computed in a similar manner for each reading, but is not the true efficiency, which was found as follows: The effective value of the alternating current electromotive force is divided into the direct current voltage. The effective e. m. f. = voltmeter reading $\times\sqrt{2}\times 2\Pi$.

The average of the alternating current voltages during half an hour was found and reduced to its effective value. The average of the direct current voltmeter reading for the same period of the run, was also found. This latter, then, divided by the effective e. m. f. gives the true voltage efficiency, as recorded in the average of results, and shown in the voltage efficiency curves.

The data for one run are given in Table I, P_f standing for power factor, V. E. for voltage efficiency, C. E. for current efficiency and E. E. for energy efficiency. The values under "Average" are the mean of the set, except for the voltage efficiency, where the mean true efficiency is put down.

TABLE I.

ALTERNATING				DIRECT			PER CENT. EFFICIENCY			
Temp.	Volts	Amp.	Watts	Volts	Amp.	Watts	P_f	V. E.	C. E.	E. E.
16.0°	109.0	0.98	65	49.0	0.55	26.9	60.8	44.9	56.1	41.5
15.5	110.5	1.00	70	50.0	0.55	27.5	63.4	45.2	55.0	39.3
15.0	108.0	1.04	75	49.0	0.56	27.4	66.6	45.4	53.8	36.5
15.0	108.5	1.08	80	50.0	0.57	28.5	68.3	46.1	52.7	35.7
15.0	107.5	1.04	75	49.0	0.56	27.4	67.0	45.6	53.8	36.5
15.0	108.5	0.98	68	49.0	0.55	26.9	64.0	45.2	56.1	39.6
15.0	107.5	1.04	68	47.5	0.55	26.1	60.8	44.2	52.9	38.4
Average		1.02					64.4	50.4	54.2	38.2
16.0	108.5	3.0	265	41.0	2.20	90.2	81.5	37.8	73.3	34.1
15.8	105.5	2.7	230	39.0	2.15	84.0	87.2	37.0	79.7	36.5
15.8	106.0	2.8	265	39.5	2.20	87.0	89.0	37.3	78.6	32.8
16.0	105.5	3.0	275	39.0	2.40	93.6	87.0	37.0	80.0	34.1
16.0	107.5	2.7	230	39.0	2.15	84.0	79.2	36.3	79.7	36.8
15.5	105.5	2.8	275	37.5	2.15	80.7	93.1	35.5	76.7	29.4
15.5	105.5	2.7	235	37.0	2.10	77.9	82.5	35.1	77.8	33.1
Average		2.81					85.3	40.8	78.0	33.3
16.0	107.5	4.5	450	36.5	3.70	135	93.2	34.0	82.2	30.0
16.2	107.0	4.0	380	36.5	3.40	124	88.5	34.1	85.0	32.7
16.2	108.5	4.4	430	36.5	3.35	122	90.1	33.7	76.1	28.5
16.1	107.5	4.4	440	36.0	3.40	123	93.0	33.5	77.3	27.9
16.1	105.5	4.2	380	35.0	3.23	113	85.8	33.2	76.9	29.8
16.0	107.5	4.3	400	35.5	3.30	117	86.5	33.0	76.7	29.3
16.0	106.5	4.2	370	35.5	3.25	116	82.6	33.3	77.5	31.2
Average		4.3					88.5	38.7	78.8	29.9
15.0	104.5	5.8	560	31.5	4.45	140	92.5	30.1	76.7	25.0
16.0	103.5	5.4	510	31.5	4.30	136	91.2	30.4	79.7	26.6
16.0	104.5	5.5	550	31.5	4.45	140	95.8	30.1	81.0	25.5
16.0	103.5	5.3	505	30.5	4.25	130	92.0	29.5	80.3	25.7
16.0	103.0	5.2	495	29.5	4.15	122	92.4	28.7	79.8	24.7
16.0	104.5	5.7	465	28.5	4.40	126	78.1	27.3	77.2	27.0
16.0	105.5	5.7	495	31.0	4.39	136	82.3	29.3	77.1	27.7
Average		5.5					89.4	34.3	77.7	26.0
17.0	101.5	7.5	700	27.5	6.05	167	92.0	27.1	80.7	23.8
17.5	105.5	8.3	830	29.5	6.40	189	94.7	27.9	77.3	22.7
18.0	106.0	8.3	850	30.0	6.50	195	96.7	28.3	78.5	22.9
18.0	103.5	8.1	815	28.0	6.50	182	97.1	27.1	80.3	22.3
18.0	106.0	8.0	800	30.5	6.35	194	94.3	28.3	79.5	24.2
18.0	105.5	8.3	815	30.0	6.40	192	93.0	28.4	77.2	23.5
18.0	105.5	8.1	800	30.0	6.25	188	94.3	28.4	77.7	23.5
Average		8.1					94.5	31.2	78.7	23.3
19.0	103.5	11.9	1,190	27.5	9.20	253	96.6	26.6	77.3	21.3
20.0	104.0	11.8	1,180	27.5	9.35	277	96.0	26.4	79.3	23.5
20.0	102.5	12.4	1,230	27.5	9.65	265	96.9	26.8	77.8	21.5
20.5	103.0	12.0	1,160	27.0	9.35	253	93.8	26.2	77.9	21.9
20.5	101.5	11.8	1,150	27.0	9.35	253	96.0	26.6	79.2	22.1
21.0	101.5	12.3	1,230	27.0	9.60	259	98.5	26.6	78.0	21.0
21.5	104.0	12.3	1,240	27.5	9.50	261	97.0	26.4	77.3	20.9
Average		12.1					96.4	29.9	78.1	21.7

The power factor rises rapidly at first from its starting point at 64 per cent., and then increases slowly, reaching a value of 96.4 per cent. at the end. The current rises rapidly from the initial value of 54 per cent., and then remains practically constant at 78 per cent. The voltage efficiency falls off from 51 per cent. at the beginning to 30 per cent. at the end. The energy efficiency drops from about 38 per cent. to about 22 per cent. These results are shown graphically in Fig. 1.

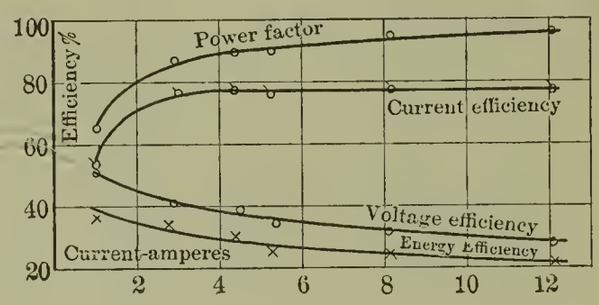

FIG. 1.

The current carried in this run was quite heavy, over 12 ampères on the alternating current side. In spite of this the tubes showed no signs of wear whatever and were apparently in as good condition as when they were first put into operation, indicating that the life of the tube under ordinary conditions would be quite long.

Some of the results were quite unexpected. A leakage current would, of course, account for a low current efficiency at low current; but it is very surprising to find the current efficiency rising rapidly to about 80 per cent. in all the runs and then remaining practically constant. So long as one assumes the existence of mechanical valves a heavy leakage current is not unreasonable; but we do not believe in valves any more. We have not yet had time to make tests on the influence of depolarizers on the current efficiency, but we hope to do this before long.

The low energy efficiency is due to the low voltage efficiency. The internal resistance of the rectifier was not determined. An examination of the current-voltage curve shows that this is not a straight line. We have, therefore, a changing resistance, a changing electromotive force, or both. The loss in voltage cannot be due solely to the internal resistance of the rectifier, this being not over 5 ohms. There is apparently a counter-electromotive force which increases with increasing current, and which has

a value of 50 to 60 volts, over two-thirds of the experimental range. This is probably due to the condenser action of the film. Unless this can be done away with the usefulness of this type of rectifier is limited to cases in which current efficiency is the sole item to be considered.

The general results of this paper are:

1. Water-cooled aluminum electrodes in a phosphoric acid solution are satisfactory mechanically.

2. A current efficiency of 75 to 80 per cent. can easily be obtained over a fairly wide range of current.

3. Under the conditions of the tests, the voltage efficiency of the aluminum rectifier may be taken as 30 to 35 per cent., and the energy efficiency as 20 to 30 per cent.

4. With increasing load the power factor rises rapidly to above 90 per cent.

5. The chief cause of the voltage loss is not the internal resistance of the rectifier. The results can be explained by assuming a counter-electromotive force increasing with the current and having a value of 50 to 60 volts over part of the range studied.

Cornell University.

DISCUSSION.

Prof. Burgess: At the first meeting of this Society, Mr. Hambuechen and I presented a paper giving the results of an analytical study of the losses of the aluminum rectifier. Our conclusions were derived from curves of pressure and current obtained by measuring instantaneous values throughout the alternating cycle. From these curves a more accurate analysis of the loss can be made than is possible with the ordinary indicating electrical instruments, and in addition to this fact such instruments are inaccurate when used on the distorted wave forms which are being measured. From the curves thus obtained it was possible to estimate how much of the inefficiency of the rectifier was due to leakage, and how much to resistance. Various investigators, including Dr. Bancroft, have stated that the opposition of aluminum to the flow of current is due to a phenomenon similar to polarization rather than to resistance. In our measurements

the only counter electromotive force which could be found was not greater than one or two volts, being equal to the ordinary pressure produced by aluminum in contact with an electrolyte.

In regard to the power factor, it is natural to expect it to be low with small load and to increase as the current delivered by the rectifier increases. In the arrangement of cells, according to the Graetz method, we have an equivalent of a condenser, and this being so, a certain amount of capacity current flows through the condenser and the power factor of the apparatus is low when on open circuit. As the current flowing through the translating devices is increased, the condenser current then becomes a smaller percentage of the total current and the power factor therefore rises. In regard to the fact that the current efficiency reaches a constant value as the load increases, this appears to be due to the increase of leakage current with the increase of current delivered. Assuming that there is a certain valve action exerted by the film on the aluminum anode, this increase of leakage is explainable by assuming the valves to be open to an extent proportionate to the amount of current flowing toward the aluminum, and upon reversing the direction of pressure a proportionately larger amount of leakage current must flow towards the solution to close the valves.

The statement is made that sulphuric acid can not be used as a solution for the rectifier, but I would like to point out that Mr. Hambuechen has found that with rather concentrated sulphuric acid very good results can be obtained so far as rectification is concerned. It cannot, however, be used practically for very evident reasons.

Mr. Carl Hering: In the abstract which Dr. Bancroft read, he did not make it clear whether the 30 per cent efficiency was true efficiency or only apparent efficiency; that is, whether there was an actual irrecoverable loss of 70 per cent of the true energy, or whether the output in true energy was compared with the input in apparent energy obtained by multiplying the volts of the alternating current by the ampères, regardless of their difference in phase. I believe it has been established that such an apparatus produces a phase shifting, and that therefore the input in volt-ampères does not represent true energy.

If the inefficiency is due to a counter e. m. f. it would be inter-

esting to know what form of energy this e. m. f. represents; that is, whether the energy is thermal, as it would be in a thermal couple, chemical as it would be in electrolysis, mechanical as it would be in a motor, magnetic as it would be in induction, etc. In some of these the loss in energy is real, in others only apparent. In some the loss is unavoidable, while in others it may not be.

There is another point to which I wish to call attention. Whenever it is necessary to send a stream of water through any conducting part of an apparatus, such as the electrode, that part becomes grounded, which seriously affects the practicability of the apparatus.

PROF. BANCROFT: The efficiency given was the apparent efficiency —that is, the ratio of the values given by the direct-current instrument to the alternating-current instrument. The direct-current ammeter was checked by means of the copper voltameter, and its readings were fairly accurate. The direct-current voltmeter could not be checked in any satisfactory way and was taken as approximately accurate. I do not believe there was any error in the instrument which would account for the 60 or 70 per cent. loss. I have no doubt that the 30 per cent. efficiency may be wrong by 3, 4 or 5 per cent. I have been very careful in the paper to say merely that we are dealing with an apparent counter electromotive force, not discussing what that actually is. The essential point for my purpose was, that it is not due to resistance in the cell. Now as regards the leakage of the current, it is a very simple matter to make an hypothesis if you assume, as Mr. Burgess does, the existence of valves. To my mind the work done in England, since Mr. Burgess' paper was published, has rather exploded the hypothesis of valves, and personally I am not prepared to admit that his photographs have the significance that he attributed to them. In fact, I do not suppose he would attribute the same significance to them now that he did at the time they were made.

PROF. BURGESS: Dr. Bancroft is just as much in error in assuming that I have changed my former belief as to the valve action as I believe him to be in some of the conclusions he has arrived at regarding the rectifier action. Our photographs to which he refers were simply the rough means of graphically representing the observations upon the "valves." The perforations can be readily observed by means of the microscope, and by this means

it can be seen that the size of the openings vary under varying conditions of current. The conclusions given were the interpretations of experimental observations and not hypotheses.

PROF. BANCROFT: The photographs represent facts; the interpretation of them may be objectionable. Mr. Burgess' idea, as I understand it, is that the efficient current flows through these perforations. My idea is that the efficient current flows through the semi-permeable films. I consider that the perforations observed by Mr. Burgess are merely points where the film has broken down and ceases to work. They are not an essential part of the process.

PRESIDENT CARHART: We have here widely divergent opinion, it strikes me. It is evident there is work to be done yet among the rectifiers. We hope to have this subject continued at some subsequent meeting of the Electrochemical Society.

A paper read at the Sixth General Meeting of the American Electrochemical Society, held at St. Louis, Mo., September 16, 1904.

SOME ASPECTS OF APPLIED ELECTROCHEMISTRY.

By Woolsey McA. Johnson.

I have headed this short and somewhat fragmentary paper, "Some Aspects of Applied Electrochemistry." Perhaps the title would be more appropriate were it given as "Commercial Aspects of Electrochemistry." It is not crass and materialistic to look upon any applied science purely in its industrial aspect. A metallurgical process should first of all make money for those who have put their capital in the enterprise. The late Prof. Eggleston, of the Columbia School of Mines, defined "metallurgy as the art of making money out of ores." Thus, it is with any electrochemical proposition that the test of the process is its commercial efficiency. A process that does not fall in this category is as sad a sight as an abandoned New England farm. It has come into an existence for which it was never intended. A deserted smelter connotes to one's mind a feeling of sadness for the misplaced and misdirected energy. Whereas, on the other hand, to me at least, a well managed and efficient plant like the Homestead works of the Carnegie Steel Co., or one of the large electrolytic copper refineries, has something grand and lofty about it, like a play of Shakespeare's, or an opera of Wagner's.

Some old-fashioned people have the privilege of ridiculing these views, but a deep insight into the question should convince anyone that these people are wrong. Viewed in its widest relations, practical science is not only compatible with the use of the imagination, but for the greatest development in this line the highest imaginative and creative powers are necessary.

Now, there are certain principles of economics and certain principles of applied science which hold good for any branch of practical work. Let us consider, for example, the present state of what may be termed straight metallurgy. Even a cursory attention to this will show that the metallurgist combines different agents and different forms of apparatus to produce his desired

effect, to wit: large production with high recovery of values and a pure product. He is also under the stress to do this commercially. Thus it will be seen that the laws which govern metallurgical operations are really, when viewed in perspective the combination of certain scientific and economic truths. Thus it may be said that applied science amalgamates two studies, economics and natural science. We will endeavor in a brief manner to give some particular illustrations of these general views.

One of the first things apparent in starting up any new proposition that is to compete with an old and established process, is that it is of prime importance to know the defects and good points of the old business. The question of the cost of raw material, the cost of treatment per ton of raw material, the usual losses, the purity of the product, which is demanded by the present market should be known with exactness. Such a knowledge will show the weak points of the old metallurgy, and many a foot-ball game has been won by hammering at a weak tackle. The new proposition should make an attack on the weakest point. For instance, we have heard much in the past two years about the so-called developments in the electrometallurgy of iron and steel. By a sort of natural evolution it is seen that the processes which have been selected as survivals of the numerous attempts have cast on the weakest spot in the present metallurgy of steel. In the manufacture of crucible cast-steel, the cost of fuel, cost of crucibles, and high labor-charge per ton of output makes an expensive product. This expensive product holds its market solely and simply because of its purity. With crucible cast-steel, quality is the desideratum. It is self-evident from the nature of electrical heating with larger units, durable furnaces, low charge of labor per ton of product, ease of control over the purity of the product, that here is the first chance for a marked victory of the electrical method over the old style of metallurgy. The fact comes out in bold relief. Somewhat a similar prediction as this was made by me at a meeting of our Society in 1902, at Niagara Falls. It is not unpleasant to know that the course of events has shown that the prediction is being verified by history-making events at the present time.

The second point which should be brought out is that not only should the present status of the old process be known, but also

a keen forecast should be made as to what improvements the old process is susceptible of. This was ably exposited in an article "On the Contact Acid Process," in the *Electrochemical Industry,* for September, 1904. Here the anonymous writer shows that under the stimulus of competition from the new contact process for making sulphuric acid, the old process has been improved greatly, as regards consumption of nitre and pounds of acid made per cubic foot of chamber space, etc. A meek and timid man will make a good fight if pushed to a corner. So capital will spend thousands of dollars in making changes in plant and process if it is seen that the life of the company is threatened. Where before suggestions as to improvement from the technical force were thought by the head office, to say the least, in distinctly bad taste in times of complacent prosperity, it is soon seen in the period of war that new ideas and reforms are quite welcome.

It is hardly necessary to give any extended illustrations of this principle, but it comes up to a person as a dictate of common sense that the new process should have a good margin over any possible future cost of production of the old process. The most successful nations have "a preference, as a race, for fighting ten to one." So, too, with applied electrochemistry, the battle should be fought along the line of least resistance.

It is a truism to remark that any electrochemical process is doubly strong if it combines the best part of the old metallurgy with something new of its own. A principle of practical metallurgy is that for producing the desired results, two, three or even many more treatments are made to attain the end results. For instance, in the treatment of copper ores in Montana, we have first, very cheap mechanical concentration by water, next smelting in regenerative reverberatory furnaces, or the "roaster and blast-furnace" treatment to a 50 per cent. matte. Next bessemerizing in the copper converter to blister copper, then refining in the reverberatory refining furnace to set copper and finally electrolytic refining.

These metallurgical reactions can be classed as roughing reactions, intermediate reactions, or finishing reactions. The meaning of the terms is self-evident.

The reason for the fact that we have several reactions quite often is that a reaction will work very cheaply and without undue

loss if it be not pushed to too far an extreme. It then becomes expensive both in operation and in the large losses ensuing. Now, for the finishing reaction, for the last part of the work a more expensive reaction can be used which gives low losses and pure products. Examples of this principle are seen in every metallurgical works. For instance, in its simplest and baldest form is seen in unloading coal or ore from a barge. Here 90 to 95 per cent. can be removed by mechanical means. The last 5 or 10 per cent. must be unloaded partly by man and wheelbarrow. Again, in the copper work it is not practical to make in the matting process a matte running over 50 per cent., for with a 60 per cent. matte the slags would be so high in copper that they could not be put over the dump. Also, in roasting a pure nickel matte to a dead oxide, it is very cheap and easy to reduce the sulphur to half of 1 per cent. in a mechanically-operated roasting furnace. It is then good practice to use a special roast in hand reverberatories to bring the sulphur to .02 per cent. The last operation is expensive, and would prohibit the process if it were attempted to remove all of the 400 pounds of sulphur in the matte by its means. But it is cheap and efficient for the last 10 pounds remaining after the first treatment. *The principle can be stated that usually a combination of reactions, each suited for its own duty, produces the cheapest result.* This general principle is one which has been often and should always be applied in an electrochemical proposition. For instance, in the electrolytic refining of copper the electrolytic treatment is the last and finishing reaction. Many attempts have been made to use anodes of matte or ore. But only failure has been met with in these attempts. The anode tried has always been purer after each failure. Now at the present time the practice is to use an anode of refined copper where silver is the chief impurity. In this connection it might be noted that the last traces of arsenic, antimony, etc., present in blister copper, could not be removed in anything like the efficient manner as they are done in the electrolytic treatment. History shows that in electrolytic copper refining the cheapest method has been found to use the prior methods for the roughing reactions and to put on the finishing touches of the refining in the electrolytic bath.

Consider any possible future developments in the electrical treatment of nickel material. The alkaline sulphide treatment

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is very cheap in making a nickel matte, containing about 1 per cent. of copper. To remove the last 1 per cent. of copper by this method is done at a great expense. Just here it is possible to apply an electrical method and cheapen the process. In all probability future developments in the electrometallurgy of nickel will be along these lines.

Another consideration is that it is often good business to push a plant to its maximum capacity with high losses, but with an increased output. For instance, in the zinc business, it might be possible to make a charge of roasted ore and reducing material of such a nature that the losses in smelting are very low. But one result of the improved smelting is seen on the cost-sheet in the increased cost of producing smelter. The old golden mean must be aimed at and the charge should be made not for the satisfaction of the metallurgist, but for the purpose of making cheap metal. This general principle was brought out quite clearly by Walter Renton Ingalls, in a recent issue of the *Mining Magazine.*

In a case where the electrochemical proposition enters a radically new field conditions are much changed. New products, like carborundum or graphite, mean that a market must be worked up by skillful advertising along lines which show that their possibilities are great. I cannot speak from any great experience in this, for most of my work in the electrical field has been done in connection with established smelting plants.

In closing this paper, which is so imperfect that it must be apologized for, because a very short time was given me by the committee for its preparation, I might make a few general remarks about the subject. The modern view of esthetics is that the test of any object is its efficiency. A thing is considered beautiful by the human mind because it connotes in the human mind the sense of efficiency. By efficiency being meant ability to do its duty well. We have in the vista of the brain a dim idea of this efficiency. So, too, with a metallurgical process. A beautiful process is one that does its work well and cheaply. It may be hoped that the short paper on the characteristics of electrochemistry and metallurgy, and the examination of the question of why successful process succeed, will help somewhat those of us engaged in practical work to an easier and better fulfillment of our wishes.

A paper read at the Sixth General Meeting of the American Electrochemical Society, held at St. Louis, Mo., September 15, 1904.

THE USE OF CARBON FOR THE STUDY OF TEMPERATURES IN THE ELECTRIC FURNACE.

By F. A. J. FitzGerald.

In the discussion following his interesting paper on "The Reduction Temperature of Zinc Oxide," read at the Washington meeting of the American Electrochemical Society, Mr. Woolsey McA. Johnson referred to some work I had done on the use of carbon in determining temperatures in the electric furnace. The study of this subject is unfortunately incomplete, but since it has been hinted at, it may be well to give some details of the observations on which it is based.

It is a well-known fact that several of the physical and chemical characteristics of carbon undergo marked changes when that substance is heated to high temperatures. When heated to the highest attainable temperatures the carbon is converted into graphite, which has different physical and chemical characteristics from those of amorphous carbon. If, however, amorphous carbon is heated to high temperatures well below that at which graphite is formed, physical and chemical differences in its characteristics are observed. In general, the changes produced by heating to high temperatures are: increase in density; increase in heat conductivity; decrease in electrical resistivity; increased resistance to oxidation when heated in oxygen; increased resistance to the disintegrating action of certain solutions. It is by taking advantage of the first of the physical changes produced in carbon by high temperatures, viz: the change in density, that a useful method for the study of temperatures in the electric furnace is found.

A simple experiment illustrates the increase in density following increase in the temperature to which carbon has been submitted. Petroleum coke is ground to a fine powder, mixed with tar or pitch which acts as a binder, and moulded in the form of a rod. The rod is introduced into an iron pipe, closed with a cap at both

ends. The whole is heated gradually to dull redness and kept at that temperature for some time so as to drive off volatile matter. Then one end of the iron pipe is heated to a high temperature, but is so protected with asbestos or some other suitable heat insulator that there is a gradual fall of temperature along the pipe. After cooling the rod is removed from the pipe, cut up into sections and the densities of the sections determined. If this is done it will be found that the densities of those sections of the carbon are highest which have been raised to the highest temperature.

It is of course understood that the density meant is the *real* density. The apparent density would vary with the conditions under which the test carbon was moulded.

If carbon is raised to still higher temperatures by heating it in an electric furnace, the density increases until finally the carbon is converted into graphite and a point reached where there is no further increase in density. It is not to be understood that after complete conversion into graphite there is no further increase in density, because the indications are that even after complete conversion there is an increase in density up to a certain point. Complete conversion of carbon into graphite is detected by means of Brodie's reaction with nitric acid and potassium chlorate, as used by Berthelot[1] and Moissan[2]. It has been found that even after all traces of amorphous carbon have disappeared there is still an increase of density with increase of temperature.

This was shown by the following experiment. A carbon rod was heated to the graphitizing temperature at one end and then cut up into sections, which were examined for density. One of these sections was found to have a density of 2.184 and treated with Brodie's mixture was converted into graphitic oxide without showing any trace of amorphous carbon. Another section which had been raised to a higher temperature had a density of 2.192 and was also converted into graphitic oxide, although the conversion was not so easy as with the other specimen. This would indicate that even after conversion into graphite there is an increase in density with increase in temperature.

In this connection Moissan's experiment with a specimen of

[1] Annales de Chimie et de Physique, Serie 3, Vol. xix, p. 392.
[2] "Le Four Électrique," Paris, 1897, p. 70.

Ceylon graphite is interesting. He found that this graphite began to form graphitic oxide at the first treatment with Brodie's mixture. He then heated the graphite to a high temperature in his electric furnace, after which it required three treatments with Brodie's mixture before conversion into graphitic oxide began.[1]

The changes in density obtained by heating carbon to various temperatures are illustrated by the following experiment. A mixture of powdered petroleum-coke and pitch was moulded in the form of a rod and baked at a dull red heat for about ten hours. The rod was then broken up and specimens were heated to various temperatures. The densities of the specimens were determined by means of a specific gravity bottle, alcohol being used as the liquid in the bottle, since it wets carbon much more readily than water. A Sprengel pump was used for removing the air from the pores of the carbon. A series of determinations were made to get a measure of the accuracy of the density determinations, with the result that the percentage average deviation was found to be 0.044. The results obtained are given in Table I, where the densities are those of the carbon at 20 degrees compared with water at 4 degrees.

TABLE I.

Specimen	Temperature	Density
1	Dull redness	1.9141
2	Above melting point of $CaCl_2$ below that of Ag.	1.9612
3	Above melting point of Ag.	1.9853
4	Above melting point of Cu., below that of cast iron	2.0061
5	Above melting point of cast iron	2.0363
6	Heated in platinum crucible over blast lamp	2.0585

In heating Specimen 6, the carbon was packed in alumina, contained in a small platinum crucible, heat radiation being diminished as much as possible by a cylindrical shield of asbestos board.

In the course of numerous experiments it was found that the time of heating to any definite temperature had an effect on the density. This was to be expected, as Moissan has shown the

[1] "Le Four Électrique," Paris, 1897, p. 92.

influence of time on the polymerization of carbon.[1] A translation of his remarks on this point is as follows:

"With lampblack purified in this way we were able to show clearly the influence of temperature on the polymerization of that elementary substance. For that purpose the following experiments were made:

"1. Lampblack was heated in a small porcelain crucible for five minutes with a blast lamp, to a temperature of 910 degrees. After heating it was not attacked by the chromate mixure (potassium bichromate, 16 grammes; sulphuric acid, 100 grammes) till heated to a temperature of 90 degrees, and combustion in oxygen began at 440 degrees.

"2. Heated a specimen at the same temperature for three hours. Attack of the new specimen by the chromate mixture began at 95 degrees, and the temperature of combustion in oxygen rose to 476 degrees. Its density was now 1.87 (original density was about 1.78).

"3. After six hours heating the lampblack was attacked by the chromate mixture at 99 degrees, and burned in oxygen at 506 degrees. Thus the polymerization of carbon, by the action of heat, at a given temperature, is not instantaneous but continues with time."

In order to find out to what extent the time element entered into the increase in density produced by heat, experiments were performed, the results of which are given in Table II. This table also gives determinations of the loss in weight after heating. The first loss given is probably partly volatile matter and partly oxidation; the remainder are probably due to oxidation.

TABLE II.

Time of heating. Hours	Temperature	Loss, per cent.	Density at 20° Water at 4°
20	Dull Red		1.9141
1	815°—830°	1.79	1.9415
8	815 —830	0.83	1.9536
6	815 —830	0.31	1.9610
6	815 —830	0.58	1.9602
0.1	Blast Lamp	0.79	1.9847
0.1	" "	0.27	1.9935
0.5	" "	0 32	2.0441

[1] "Le Four Électrique," Paris, 1897, p. 58.

It will be seen from this table that after heating for fifteen hours to a temperature of 815 degrees to 830 degrees, there is no further change in density when the heating is continued for six hours more. As there was no means of getting an exact temperature adjustment when heating over the blast lamp the experiment at that temperature was carried no further than is shown in the table.

In making experiments on the change of density produced in carbon by heating, it is important to remember that the density corresponding to any definite temperature varies with the kind of carbon used. Thus, if carbon rods composed of lampblack and petroleum coke, respectively, are heated to the same temperature, for example, about 1,000 degrees to 1,200 degrees, their densities will be different; the density of the lampblack will be about 1.75, while that of the petroleum coke will be about 2.00. When both are heated to the temperature of graphitization their respective densities will be about 2.05 and 2.20.

In certain forms of electric furnaces the determination of temperatures in the interior is by no means easy, and yet the importance of obtaining some notion of the temperature is great. In some cases the change of density produced in carbon by the temperature may be used to advantage in studying the temperature conditions in the furnace. To illustrate this, some experiments made in conjunction with Mr. Bennie at our laboratories in Niagara Falls, may be described.

In one of these experiments the furnace consisted essentially of a long fire clay oven, divided into several compartments. The oven was heated from above and below by heating resistances connected with the terminals of the furnace. One of the vertical sides of the oven was permanently closed, the opposite side being open so that access to the interior of the oven could be obtained. It was important that the temperature in the interior of the oven should be perfectly uniform. To test whether this condition was fulfilled one of the compartments was filled with sand and specimens of carbon placed at various points. The side of the oven was then built up with a double-brick wall. The furnace was run for about sixteen hours. After cooling, the compartment was opened, the test carbons removed and their densities determined. The results obtained were as follows:

Position in compartment.	Density.
Closed end	1.9685
Centre	2.0333
Open end	1.9686

This plainly showed that there was a great difference between the centre and outer ends of the compartment. In spite of the thick walls of fire-brick the heat losses at the sides of the furnace were sufficient to prevent the temperature of the outer ends of the compartment from rising above the melting point of silver, although the centre of the muffle was about the temperature of the fusion of cast iron.

Other experiments we have made in the same direction have convinced us of the great importance of efficient heat insulation in electric furnace work. This is important for two reasons; first, because the generation of heat by electricity is expensive; second, because, as shown in this experiment, the distribution of temperature may be seriously affected by insufficient heat insulation.

In another experimental furnace a long heating resistance was used. The resistivity of different parts of the resistance material were roughly adjusted so as to make the drop of voltage along equal lengths of the resistance the same. In this way the amount of heat generated along equal lengths of the resistance would be equal, and *ceteris paribus* the temperature at different parts of the furnace would be the same. One of the points to be determined was whether the adjustment of resistivity was sufficiently accurate to give this result. Test carbons were placed at various points and after running the furnace the densities of the test carbons were determined. The results obtained for six sections of the furnace were as follows:

Section of Furnace.	Density of test carbon.
1	2.1244
2	2.1433
3	2.0970
4	2.0963
5	2.0885
6	2.1156

This showed very plainly a great variation in temperature, and

it may be remarked that the variations corresponded with the differences in resistivity of the heating resistance.

In using carbon for the study of temperatures in the electric furnace care must be taken that errors are not introduced by the presence of other substances. At relatively moderate temperatures errors of this kind are improbable, but where very high temperatures are used various heavy substances, such as iron, are vaporized, and these condensing in the pores of the test carbons may seriously affect the density determinations.

Although this method of studying temperatures in the electric furnace has not been completely worked out, and has but a limited application, yet it is believed that in certain cases it is of value in experimental work, and may be of assistance to others engaged in similar electric furnace work.

FitzGerald & Bennie Laboratories,
Niagara Falls, N. Y.

A paper read at the Sixth General Meeting of the American Electrochemical Society, held at St. Louis, Mo., September 15, 1904.

ELECTROLYTIC PURIFICATION OF COBALT AND NICKEL.

By Wilder D. Bancroft.

In an alkaline tartrate solution the decomposition voltage of cobalt is about 1 volt lower than that of nickel. This promised well for an electrolytic separation of the two metals. Vortmann[1] has stated that a quantitative separation is possible in this solution but he gives no data of any sort. The matter was taken up in my laboratory by Mr. Root, who will report in detail elsewhere. Cobalt peroxide tends to precipitate at the anode. This can be overcome pretty well by making the anode current density high or by adding a few drops of concentrated nitric acid to the solution. In the latter case there is still a deposit at the anode, if the current density is low, but it consists practically entirely of nickel peroxide. With a Classen dish as cathode and a potential difference of 1.9 to 2.0 volts between the electrodes a good deposit of cobalt is obtained which gives no test for nickel. Some cobalt is always left in the solution. If the voltage be raised to take out the last traces of the cobalt, some nickel is also precipitated. Heating the solution makes matters worse. The addition of potassium iodide, as recommended by Vortmann, is quite unsatisfactory. The trouble is due in part to the oxidation of cobaltous salt to cobaltic salt at the anode. Addition of hydroxylamine sulphate, hydrogen peroxide, formaldehyde, or sodium bisulphite helps a little, but does not enable one to get out the last traces of cobalt in any reasonable time. Since no one would be willing to spend a week on a single analysis, this part of the subject was dropped for the present.

Experiments were then made on electrolytic purification to see whether the bulk of the cobalt could be obtained free from nickel and the bulk of the nickel obtained free from cobalt. Nickel peroxide precipitates more readily the more carbonate and the less tartrate there is. As cobalt peroxide tends to come down with

[1] Monatsheft, **14**, 536 (1893).

the nickel, it was found best first to precipitate nearly all the cobalt, then to add sodium carbonate and electrolyze with low anode density. There are three cases to be considered: cobalt solutions, with nickel as impurity; nickel solutions, with cobalt as impurity; solutions containing nickel and cobalt, neither being present in large excess.

The salts used were crystallized cobalt sulphate $CoSO_4 7H_2O$ from the laboratory stock, and crystallized nickel nitrate $NiNO_3 2H_2O$. Neither salt was free from the metal of the other. The cobalt sulphate lost some water while being powdered and contained about 22.5 to 23.5 per cent. of cobalt instead of the more orthodox 21 per cent. This made no difference because it was only necessary to obtain metal, peroxide and solution which would pass the tests. The following tests were used in all the work:

Test for nickel in presence of cobalt.—The hydroxides of nickel and cobalt are filtered, washed and dissolved in the least possible amount of hot concentrated potassium cyanide solution. To this solution add three times its volume of strong NaOH solution, then bromine water in excess and warm. The appearance of a blackish coloration is due to nickelic hydroxide.

Test for cobalt in presence of nickel.—Solutions, if acid, are made alkaline with NaOH. Add slight excess of acetic acid, then large excess of saturated solution of KNO_2. The appearance of yellow precipitate upon standing over night in a warm place indicates traces of cobalt.

In the first run 150 cc. of solution contained

5.01 g cobalt sulphate	10 g sodium potassium tartrate.
0.505 g nickel nitrate	3 drops hot conc. HNO_3

50 cc. caustic soda (sp. g. 1.3).

A Classen dish was used as cathode and a needle anode. The solution was electrolyzed thirty hours at 20 degrees and 2 volts. The cathode deposit weighed 1.069 g, and gave no test for nickel. The solution still contained cobalt. A clean cathode was substituted and the run continued for twenty-four hours more. The cathode deposit weighed 0.058 g and was free from nickel. The solution gave only a faint test for cobalt. A platinum dish was now made anode and a rotating platinum disk the cathode. After

adding 5 gNa_2Co_3 the solution was electrolyzed for another twenty-four hours. The cathode deposit weighed 0.0016 g and contained no nickel. The anode deposit did not adhere well and the solution was therefore filtered through a Gooch crucible. In this way there were obtained 0.16429 gNi_2O_3 on the anode and 0.0356 g in the Gooch. This peroxide gave a faint trace for cobalt, probably due to occluded mother liquor.[1] The solution was colorless and gave no test for cobalt or nickel. The yield is 1.1285 g of pure cobalt and 0.1998 g of nickel peroxide, containing the merest traces of cobalt. By dissolving and reprecipitating this trace of cobalt could be removed. In a second run with 5.004 g cobalt sulphate and 0.1256 g nickel nitrate, 1.1233 g pure cobalt were obtained and 0.0638 g of nickel peroxide containing traces of cobalt.

In the next run the conditions were the same as before except that the solution contained 2.0 g cobalt sulphate and 2.041 g nickel nitrate, and that the voltage was 1.9 volts.

Electrolyzed 20 hours.
Deposit = 0.2672 g Co, pure.
Electrolyzed with clean electrodes, 7 hours.
Deposit = 0.0452 g Co, pure.
Electrolyzed with clean electrodes, 17 hours.
Deposit = 0.0752 g Co, pure.
Electrolyzed with clean electrodes, 24 hours.
Deposit = 0.0478 g Co, pure.
Electrolyzed with clean electrodes, 19 hours.
Deposit = 0.0067 g Co, pure.
Electrolyzed with clean electrodes, 17 hours.
Deposit = 0.0017 g Co, pure.
Electrolyzed with clean electrodes, 48 hours.
Deposit = 0.0044 g Co, pure.
Added 10 g sodium potassium tartrate and 25 cc. NaOH.
Electrolyzed with clean electrodes, 48 hours.
Deposit = 0.0042 g Co, pure.
Electrolyzed 5 hours, with a wire gauze anode, ½ inch by 4 inches, wrapped in parchment paper. Solution stirred.
Deposit = 0.0062 g Co, pure. Only slight deposit on gauze. Solution free from cobalt.

[1] Coehn. Zeit. anorg. Chem., **33**, 9 (1903).

Added 5 gNa_2CO_3 and electrolyzed 24 hours with dish as anode and stationary disk as cathode.

Anode deposit = 0.7718 gNi_2O_3 free from cobalt.

No cathode deposit. Solution free from nickel and cobalt.

The total yield is 0.4586 g cobalt free from nickel and 0.7718 g nickel peroxide free from cobalt. The exceptional purity of the nickel peroxide is due to the fact that all the cobalt was removed before the peroxide was precipitated. It is, however, a very tedious job to remove the last traces of cobalt when there is much nickel present, over eight days in this particular case.

To test the separation of a large amount of nickel from a small amount of cobalt, a solution was taken containing 5.002 g nickel nitrate and 0.1007 g cobalt sulphate. At first a needle anode and a dish cathode were used. A voltage of 1.9 volts gave only 0.05 ampères. At the end of forty-nine hours there had been deposited 0.0102 g Co, pure. After forty-seven hours more there had been deposited 0.0042 g Co, pure. The needle anode was replaced by a rotating disk and the electrolysis continued for 2.5 hours at 1.8 volts (0.2 ampères). At the cathode there was 0.0010 g Co, pure; at the anode 0.0029 g cobalt peroxide, free from nickel. Three grammes of sodium potassium tartrate were added and the solution electrolyzed for sixteen hours with continuous stirring. The cathode deposit consisted of 0.0042 g pure cobalt and the anode deposit of 0.0011 g cobalt peroxide free from nickel. As there was only very little cobalt left in the solution, the electrodes were reversed, 5 grammes of sodium carbonate added, and the solution electrolyzed for twenty-four hours at 2.1 volts. At the cathode was 0.0011 g Co, showing faint traces of nickel. The nickel peroxide at the anode weighed 1.2561 g and 0.6439 g was obtained by filtration. This peroxide showed faint traces of cobalt. The total yield was 0.0196 g cobalt, pure; 0.0011 g cobalt, impure; 0.004 g cobalt peroxide, impure; 1.9 g nickel peroxide, containing traces of cobalt. In a second experiment there was no nitric acid in the solution and no sodium potassium tartrate was added during the run. Under these conditions the cobalt and nickel peroxides come down together and there is no satisfactory separation.

No experiments have yet been made using a diaphragm.

The general results are:

1. It is possible to obtain nickel and cobalt pure from an alkaline tartrate solution if one is willing to take the time and pains.

2. The difficulty is due in part to the formation of cobaltic salt in the solution.

Cornell University.

DISCUSSION.

MR. SADTLER: Mr. Bancroft, I was wondering whether if an antimony anode were used with potassium tartrate present, tartar emetic might not be formed and in that way prevent the evolution of oxygen at the anode, thus preventing reoxidation of the cobalt. I suggest this merely as an off-hand example of the use of a soluble anode.

PROF. BANCROFT: We thought of using a soluble zinc anode, but there seemed to be danger of precipitating cobalt on the zinc. I have never made any experiments with an antimony anode, and I do not know just how it would behave, but I should expect that it would either have the same disadvantage, or else it would not work at all. It is essential to have a high current density at the anode when you wish to keep up the cobalt peroxide. When it comes to precipitating the nickel later on, the conditions are reversed, and we use a large anode and small cathode, so as to get the nickel peroxide down in some satisfactory form.

A paper read at a meeting of the Philadelphia Section of the American Electrochemical Society, December 5, 1904.

ELECTROCHEMICAL EXHIBITS AT THE LOUISIANA PURCHASE EXPOSITION, ST. LOUIS, 1904.

By S. S. Sadtler.

A description of everything of electrochemical interest at St. Louis is beyond the scope of this paper. A brief description of the products of some of the best known industries may, however, prove of interest. It is much to be regretted that what is shown does not adequately represent the progress made in electrochemistry since the last great international exposition held in Paris in 1900. This is partly to be accounted for by the statement that chemical products in general do not lend themselves as readily towards making a display as do machinery and other manufactured articles, and partly by the fact that the past two years have not been ones of business expansion, and companies have not made the showing they otherwise might have made.

The forms of scientific research apparatus, shown in the German exhibit in the Palace of Electricity, were of great interest and the collection particularly complete. A brief enumeration of what are probably the most representative exhibits may be here given. It had been hoped to illustrate this enumeration with cuts, but these could not be obtained in time for this publication. They may be noted as follows:

Pieces of apparatus, made by Prof. Dr. F. Kohlrausch himself, including cells for measuring the resistances of electrolytes and apparatus for measurements by the Kohlrausch method.

Forms of apparatus, according to Dr. W. Ostwald, for measuring the internal friction and surface tension of liquids;[1] for measuring the critical pressure,[2] and a chemograph, complete,[3] also apparatus for ascertaining electrolytic resistance.[4]

Very interesting apparatus, devised by Dr. W. Nernst, for the

[1] Ostwald-Luther, Physiko-Chem. Messungen.
[2] Altschul, Zeitschr. f. Physik. Chem., 11, 577, 1893.
Ostwald-Luther, Physiko-Chem. Messungen.
[3] W. Ostwald, Period. Erscheinungen beiden Auflösung des Chroms in Sauren, ii, p. 36.
[4] W. Ostwald, Zeit. f. Phys. Chem., ii, 561, 1888.

determination of di-electric constants,[5] the normal hydrogen, electrode and concentration batteries.[6]

An electrometer, according to Dolazelek.[7]

Ampère manometers,[8] according to Bredig and Hahn.

Electrolytic carbon precipitator, by Dr. Cohen.[9]

Forms of apparatus for the electrochemical reduction of nitro bodies in alkaline solution,[10] for the reduction of ketones,[11] and for the electrochemical preparation of tetra chloride of lead.[12]

By Dr. Elbs and W. Schmidt.

Apparatus for the direct measuring of ion movements, according to Dr. Abegg and Steele.[13]

Di-electric apparatus, according to Drude.[14]

A very interesting exhibit also worthy of prominent mention was the electrolytic preparations of Dr. Elbs.

Sodium.—The Acker Process Co. merely exhibited five products, namely, caustic soda, bleaching powder, carbon tetrachloride (CCL_4), tetrachloride of tin ($SnCl_4$) and oxide of tin. The process whereby their caustic soda is made has been fully described in these Transactions, Vol. I, 1904, and the processes by which the carbon tetrachloride and the tetrachloride of tin are made, have not, at least have not until very recently, been fully protected by patents. In the works of the company at Niagara Falls, about 3,800 electrical horse-power are utilized. The greater part of this current is used to decompose fused sodium chloride in the electrolytic cells. A current of 9,000 ampères and 300 volts is conducted through great bundles of aluminum conductors placed in trenches under ground.

The Castner Electrolytic Alkali Co. exhibited caustic soda, made in the Castner cell, testing 99.5 and bleaching powder (38-40 available chlorine). These products are made at Niagara Falls, several thousand electrical horse-power being used for their manufacture.

[5] W. Nernst, Zeit. f. Phys. Chem., xiv, 622, 1894.
[6] W. Nernst, Zeit. f. Phys. Chem., iv, 129, 1889.
[7] Dolazelek, Verh. d. Physikal. Ges., iii, 18, 1901.
[8] Zeit. f. Electrochem., vii, 259, 1900.
[9] Zeit. f. Electrochem., ii, 541, 1895-6.
[10] Elbs & Kopp, Zeit. f. Electrochem., v, 109, 1898.
[11] Elbs & Brand, Zeit. f. Electrochem., viii, 784, 1902.
[12] Elbs & Nubling, Zeit. f. Electrochem., ix, 777, 1903.
[13] Zeit. f. Electrochem., vii, 259, 1900.
[14] Wied. Ann., 61, 466, 1897.

The United Alkali Co., of Great Britain, exhibited the following products of electrolytic manufacture: Caustic soda, bleaching powder, sodium chlorate and potassium chlorate.

The Niagara Electrochemical Co. showed metallic sodium made from sodium hydrate in the electric furnace, and peroxide of sodium and cyanide made from the sodium. Two grades of cyanide are manufactured. Cyanide of sodium and potassium testing equal to 98-99 per cent. Cyanide of potassium and a high-grade cyanide of sodium, equivalent to 125 to 130 per cent. cyanide of potassium.

Solvay & Co., Belgium, exhibited chlorate of potash and chlorine.

Aluminum and its Compounds.—There has probably been no important improvement in the manufacture of aluminum, the development being mainly in the extensions of its usefulness. Among these may be mentioned: Electric conductors, cooking utensils, automobile frames and parts, bus bars and fancy articles almost without number. An important application of aluminum is in the Goldschmidt Thermit mixture (see page 85, II).

The Pittsburg Reduction Co. displayed ingots, sheets, wire rods, tubing and a great variety of articles manufactured from aluminum. The ingots are used largely in the steel industry as a flux and a deoxidizer, and in the general metal trade for making castings and to replace brass, it being cheaper, bulk for bulk, and useful for all purposes where weight is of consequence. It also has extended uses in the shape of sheet metal.

The most interesting development in the use of aluminum is its application as conductors for electric power transmission in either solid or stranded form. For the same conductivity it has about 47 per cent. of the weight of copper, although it is 60 per cent. greater in cross section. It is also said to be somewhat cheaper, especially in erecting a line in which savings in the number of poles, insulators, etc., are taken into account, and where hauling is a factor, it manifests its superiority. The drawbacks to its use are its tendency to stretch and to expand with heat. There is probably no electrochemical product the sale of which has developed so much in the last few years.

Société Electrometallurgique Française, Froges, France, manufacture aluminum by the Heroult process. The Froges works

were the first electrometallurgical works erected in France, but the main works of the company are at La Praz, where 13,000 horse-power is available. At St. Michel de Maurienne, 5 or 6 miles from La Praz, new works are being erected, which will utilize 17,000 horse-power. A 7-ton Heroult furnace can produce 150 tons of steel per twenty-four hours from low-grade material.

This company manufactures pure alumina, carbon electrodes, aluminum ingots, plates, bars, wires, cables, tubes, etc., electric steel, ferro-chrome, ferro-silicon.

The manufacture of cast iron, ferro-nickel, copper and ferro-tungsten are amongst those contemplated.

Specimens made in the electric furnace, which were shown: Pure aluminum of 99.6 and 99.7 per cent., and various forms showing the uses in the arts; cast iron, both white and gray; ferro-nickel, containing about 40 per cent. nickel, 2 per cent. carbon and less than 2 per cent. silicon (from nickel ores); copper matte, containing 40 per cent. copper (from siliceous ores, containing 6 per cent. copper); ferro-tungsten, containing about 80 per cent. of tungsten; ferro-silicon, containing 20, 25, 30, 40 and 50 per cent. silicon; iron and steel, containing .02 to 4 per cent. carbon.

The Norton Emery Wheel Co., of Worcester, Mass., showed an artificial corundum for abrasive purposes, made by fusing oxide of aluminum in the electric furnace at their works at Niagara Falls. This product, called alundum, is said to be harder than the natural corundum.

The Carborundum Co. have recently introduced silicon, the commercial production of which is the achievement of Mr. F. J. Tone, the manager of their works. The process has not yet been described in technical literature aside from the patent specification.

This metal, which is the most abundant constituent of the earth's crust, has been taken from the list of chemical curiosities and put on the market at 35 cents a pound. There has not been sufficient time as yet to learn all the probable important uses for this product, but it has already been found useful in the casting of copper and copper alloys and in the manufacture of various grades of steel.

Carborundum, or silicon carbide, is the chief product of this company. Its manufacture, composition and uses, are well known. It is used as an abrasive and for heat-refractory purposes.

Carborundum fire-sand is a product possibly not so well known. It contains oxygen either due to free silica or else as an intermediate product in "the formation" of silicon carbide. It is formed at a temperature of 3,000 to 3,500 degrees in the electric furnace. It has a specific gravity of 2.7, is of a grayish-green color, granular, easily sintered and of low heat conductivity, and generally neutral to acids and bases.

CARBON.—Among the exhibits of carbon shown for electrode uses in primary batteries, electric furnaces and electrolytic cells, are the following:

The National Carbon Co. supplies carbon for dry cells (and it may be noted here that the main feature with regard to improvements in primary batteries lies in the grade and purity of the ingredients, including the carbons) and for electrical purposes, such as electric lights, carbon brushes, electrodes and electric furnace terminals. This company supplies the Acheson Graphite Co. with electrodes to be graphitized.

The Compagnie Française Des Electrodes, of Lyons, France, manufacture electrodes of all sizes up to 40 cm. by 40 cm. in section and 150 cm. in length, with a specific resistance of 4 to 4.5 ohms per cubic centimeter. These carbons are made of petroleum coke, carbon or anthracite, according to requirements with regard to conductivity, cost, wearing qualities, etc. The output is 4,000 tons per year.

The Acheson graphite is made by electric furnaces of 1,000 horse-power capacity. The company is now erecting additional furnaces of 2,000 horse-power. Anthracite coal, after many trials with other materials, was found to be the best raw material for the manufacture of graphite, as the silica, which must be combined with carbon as the heat is raised and which is afterwards given off, leaving graphite, should be evenly distributed throughout the carbon.

The furnaces used are long, narrow troughs with heavy carbon terminals at each end and a connecting carbon rod between. Around this rod the coal is packed, or in the case of the making of electrodes, the ready formed electrodes, of the carbon mixtures found suitable for the purpose.

The heat employed is in the first stage sufficient to form silicon carbide and finally high enough to volatilize the silicon.

Acheson graphite is made up as electrodes, motor and generator brushes, sliding contacts, bushings, stirring rods for metallurgical purposes, crucibles, moulds, etc., as well as in powdered or granular form for the manufacture of paint, stove polish, dry batteries, motor brushes, lubricating purposes, electrotyping, etc. It is furnished in four principal grades of 90, 93, 98 and over 98 per cent carbon.

Calcium Carbide.[15]—The Union Carbide Co. controls the output of calcium carbide in the United States and operates works at Niagara Falls, where 15,000 horse-power are used, and at Sault Ste. Marie, where 20,000 horse-power are required.

The carbide is made in electric furnaces of about 300 horse-power, which are circular in form, each having a recessed rim, to the top of which is bolted segmental wings. In the space thus formed two carbons are placed at the top of a wheel. The charge of lime and carbon there fed to them is fused by the arc formed by the current passing from one carbon to the other. The furnaces revolve slowly on trunnions, making an entire turn once in forty-eight hours, the fluid carbide resulting from the action of the arc as above described is thus taken out of the fusion zone and solidifies. The ingots are taken out from the lower side of the wheel comparatively cold, and from 2 to 10 inches thick. In diameter each furnace is about 10 feet. The calcium carbide made by this company is claimed to be much superior to that made in Europe, and it is claimed that the acetylene made therefrom does not need purifying.

Copper.—In order to show the present status of electrolytic production of copper, the following table is taken from an article by Prof. H. O. Hoffman, in the Transactions of the American Institute of Mining Engineers, Vol. XXXIV, "Notes on the Metallurgy of Copper of Montana," describing the plants operated by the Boston and Montana Consolidated Copper and Silver Mining Co., who exhibited at the World's Fair, a very interesting exhibit consisting of ingots of copper, silver and gold, showing the relative amounts produced by their process.

[15] Niagara Falls Electrical Handbook, A. Inst. Elec. Eng. 1904.

DETAILS OF ELECTROLYTIC REFINERIES.

	Great Falls.	*Anaconda.*
Number of tanks	312	1,400
Length " "	9 ft. 9 in.	8 ft. 2 in. inside.
Width " "	2 ft. 4 in.	4 ft. 5 in.
Depth " "	3 ft. 9 in.	4 ft. 6 in. measure
Number of tanks per set, *i. e.*, number of tanks using same solution	104	200
Number of anodes per tank	20	38
" " cathodes per tank	20	80
" " ampères per sq. ft. of cathode area	40	10
POWER—		
Number of generators	2	7
" " circuits	1	7
Ampères generated per circuit	9,000	4,000
Volts per circuit	200	60
Character of material worked	Converter, anodes.	Casting furnace. anodes.
Kind of moulds used	Copper.	Iron.
Casting machines, pattern	Walker.	Anaconda.
Converter anodes, per cent. Cu	99.1	.....
" " " " As. & Sb	0.07	.....
" " oz. Ag	56.00	.....
" " oz. Au	0.20	.....
" " per cent. scrap	8.00	.....
" " mud, per cent. Cu	41.	.....
" " " oz. Ag	7,000	.....
" " " oz. Au	18.	.....
Refined-anodes, per cent. Cu	99.27	99.25
" " " " As. & Sb	0.07	0.10
" " oz. Ag	61.14	90.00
" " oz. Au	0.22	0.50
" " per cent. scrap	5.5	7.00
" " mud, per cent. Cu	18.00	10.00
" " " oz. Ag	15,000	18,000
" " " oz. Au	38.00	100.00
SIZE OF ANODES—		
Length	35 inches.	32⅞ in.
Width	24 "	24½ "
Thickness	3 in., 2½ in.	1¼ in., 1 in.
Weight in lbs. converter	500	.....
" " " refined	632	230
No. of days corroding, refined	.....	37
" " " " converter	18	.....
SIZE OF CATHODES—		
Length	36½ in.	33 in.
Width	26 in.	11 in.
Weight of starting-sheets, lb	2½	¾, 1
" " cathodes, lb	55	100
Number of cathodes on one bar	1	4
ELECTROLYTE—		
Sulphuric acid per litre grammes	170	150
Copper per litre, grammes	42	40
Temperature at head tank, C°	64	50
Circulation per minute, gallons	6	3
DIFFERENCE IN POTENTIAL—		
Soluble anodes, per tank	.6	.3
Insoluble " " "	2.5	2.
Composition of cathode, per cent. Cu	99.95	99.96
" " " " " As.	.0012	.0009
" " " " " Sb.	.0033	.0023
" " " oz. Ag	1.0	0.25

Zinc.—Bruner, Mond & Co., Ltd., Northwich, Eng., were probably the only exhibitors of electrolytic zinc. Their product is made by a process similar to or identical with the Hoepfner process. Analysis.

	Per cent.
Zinc	99.9789
Cadmium	0.0037
Iron	0.0096
Lead	0.0072
Copper	0.0006

Claimed to be free from arsenic, although no guarantee of this is furnished.

Iron.—Besides the electric furnace iron, steels and ferro-alloys exhibited by the Société Electrometallurgique Francaise, Niagara Electrochemical Co., etc., there was a very interesting exhibit by Burgess and Hambuechen[16] of electrolytic iron, prepared in the wet way.

The Electric Reduction Co., of Buckingham, Quebec, showed:

Ferro-chrome, made from the chromite of Black Lake.

Ferro-silicon, made from silicate of iron.

Phosphide of iron, made from apatite and iron ore.

While there may be little, if any, material in this paper that will not be found elsewhere in the literature, it is hoped that this bringing together of information with regard to many of the electrochemical industries represented at St. Louis, and references to further information will be of some value.

[16] Trans. A. E. S. Vol. v. page.

PART II

PAPERS READ IN JOINT SESSIONS OF THE

American Electrochemical Society

AND THE

Fifth International Electrical Congress

ST. LOUIS, MO.

September 13 and 15, 1904

Opening Session, Section C.

Monday, September 12, 1904.

Section C was called to order Monday morning, September 12, 1904, at 11:30 o'clock in one of the section halls of the Auditorium on Olive street, by the chairman, Prof. Henry S. Carhart.

The Chair announced that in the absence of the author, Dr. George W. Patterson, Jr., of the University of Michigan, would read the paper prepared by Prof. Theodore William Richards, of Harvard University, on "Compressible Atoms." Thereupon Dr. Patterson read the following paper:

THE RELATION OF THE HYPOTHESIS OF COMPRESSIBLE ATOMS TO ELECTROCHEMISTRY.

BY PROF. THEODORE WILLIAM RICHARDS, *Harvard University.*

The nature and origin of chemical affinity, and the laws which govern its irregular manifestation are veiled in unusual obscurity. There can be no doubt, however, that the chemical elements are in some way often firmly held together in compounds, and that in the process of forming these firm combinations much potential energy is usually converted into heat or electrical energy. The mechanism of this, the most important source of power to living beings, is hard to discover.

A few years ago, it occurred to the author that since affinity binds firmly, it should also exert pressure, and should therefore tend to combat all the influences existent in matter tending to distend the substance. The mutual affinity of two elements in a compound should, therefore, tend to diminish the volume of this compound; and, other things being equal, the greater the affinity, the greater would be the change of volume and the smaller would be the final volume of the resulting compound. If this relation really held true, it should be most clearly perceptible in compressible substances; hence a number of compounds of the easily compressible halogens, chlorine, bromine and iodine were studied with regard to this possible relationship. It was discovered that, in general, the volume of a solid chloride or bromide was much less than the sum of the volumes of the metal and the liquid chlorine or bromine entering into its composition; and, moreover, the more energetic the reaction, the greater was the change in volume during its progress.[1] That is to say, a great affinity evidently caused a great contraction. Subsequently it was found that this parallelism

1. Richards *Proc.* Am. Acad., Vols. 37, 38. *Zeitschr Phys. Chem.*, Vols. 40, 42.

In this comparison the heat of reaction was taken as the measure of chemical energy. It was shown that where no great change of heat capacity occurs during the reaction this is a permissible proceeding — that is, under these conditions Berthelot's "rule of maximum work" holds nearly true.

of intensity of reaction and magnitude of contraction had already been noticed in some cases as long ago as 1881, by Müller-Erzbach, and later by Traube, and by Hagemann, all quite independently of one another.[2]

The relation, although in some cases quite striking, is in other cases concealed by other circumstances, especially by the differences in compressibility of various substances. It has recently been shown that, as one would expect, the more compressible the element, the greater the contraction which occurs for a given expenditure of energy.[3] The demonstration of this additional fact is a strong evidence that affinity really exerts pressure, and that the volume of a liquid or solid is dependent upon the intensity of this pressure. The attraction of cohesion also was shown to exert a similar effect. When corrected for the compressibility of the factors in a reaction, and for the cohesion of both factors and products, the correspondence between the output of chemical energy and the change of volume during the reaction becomes so close as to leave little doubt as to the fundamental nature of the relation. In any attempt to penetrate further into the reason of these facts, some assumption, avowedly hypothetical, must be made concerning the ultimate nature of material. For the present purpose the atomic hypothesis furnishes the most convenient foundation.

The further question now presents itself:— What is that which is compressed by this pressure? In other words, what is the distending tendency in solids or liquids? Does the pressure of affinity simply restrict the vibrations of separate hard particles in an empty space, or is the atom itself compressible? It seems to me that the former usually accepted hypothesis does not sufficiently explain the difference between a solid and a gas. Moreover, even at the lowest attainable pressures, where the thermal vibration must be scarcely perceptible, ice occupies only about half the volume of the solid oxygen and hydrogen from which it may be made. Such a large change in volume seems incomprehensible, if it is imagined to be due to a restriction of thermal vibrations already almost infinitesimal. The undoubted variation of the quantity b in the equation of van der Waals, and many other facts, point in the same direction. In short, all that we really know of the volume of the atom must include the compressible environment which

2. Müller-Erzbach. *Berichte* d. d. Ch. G. *14*, 217, 2043 (1881). Traube. Raum der Atome (Stuttgart), 1899. Hagemann (privately published by Friedlander), 1900.

3. Richards. *Proc.* Am. Acad., *39*, 581 (1904).

seems always to surround it, for we have no direct means of knowing how that which we call material is distributed within this space — the imaginary, hard particle surrounded by an imaginary empty space is pure assumption. It seems to me, therefore, more rational to admit that the compressible environment is an essential part of the atom, or, in other words, that the atom itself is compressible. The other alternative, of imagining the atom to be incompressible, and the empty space alone to change in volume, has often been chosen simply because its mathematical handling is a simpler proposition; but ease of mathematical treatment is no evidence of verity in such a case. The need of an empty space for freedom of vibration in order to afford the chance of a mechanical explanation of heat in solids would at first seem to be an argument in favor of the separate hard particles, but it must be remembered that if the atom were elastic and compressible, its interior could vibrate even if its surface were bound. Hence this support also falls to the ground, and the theory of compressible atoms stands at least on the same level as its older brother, as far as probability is concerned.

It may be pointed out that the hypothesis of compressible atoms is entirely consistent with the corpuscular conception of atomic structure which is so popular today, or is equally consistent with an hypothesis which imagines all atoms to be built of the same continuous, compressible medium of which the corpuscles (if indeed they exist at all) are smaller aggregations.

The purpose of this paper is not, however, to discuss all the arguments which support the hypothesis of compressible atoms. Enough have now been brought forward to show that the hypothesis is a reasonable one, not to be cast aside without further thought. Whether or not it may be a nearer approach to a definite picture of reality is a question of less importance than that concerning its ability to suggest new experimental work, and thus to lead to new generalization based upon fact. Hypotheses are temporary in their very nature; it has been said that science is being built up of stones taken from their ruins. Perhaps it might rather be said that hypotheses are the scaffolding which the scientific man erects around the growing solid structure, enabling him to build more swiftly and freely. Danger can arise from the use of such temporary assistance only when the builder confounds the temporary with the permanent, and builds one into the other in such a way that the collapse of one injures the other; or when the scaffolding is so

badly constructed as not to bear a reasonable weight for a reasonable time.

The purpose of this paper is to show that this particular hypothesis, dealing as it does with very intimate relations of energy and material, is not without suggestiveness to the electrochemist, and hence also to the electrician.

Theoretical Electrochemistry may be divided into two closely related sections — that which treats of the phenomena at the electrode, and that which treats of the phenomena in the unchanged electrolyte. The former of these sections is the more important practically, and is likewise a more certain domain theoretically.

In the first place, then, one may ask:— How would a compressible atom behave on leaving an electrode and going into solution as an ion? It would then be attacked by an entirely new set of affinities, being in its new position surrounded by molecules of the solvent instead of by atoms similar to itself, and these new affinities exerting new intensity of pressure would be expected to change its volume. Moreover, the solvent, being itself in part exposed to new internal pressures, would also change in volume. As a matter of fact, a marked change of volume is always observed when a positive and negative element go into solution in the ionized condition. For example, a litre of a normal solution of potassic chloride occupies 43 millilitres less space than the solid potassium, liquid chlorine and water from which it may be made; the change of volume in the case of common salt is 31 millilitres, and that in the case of lithic chloride 17 millilitres. Potassic bromide in the same way gives a contraction of 33 millilitres. Among these similar compounds, and in many other cases, it usually appears that the greater the electrical potential afforded by the double ionization, the greater the change of volume; also, the greater the compressibility of the elements concerned, the greater the change in volume. It is worth while also to call attention to the fact that these changes of volume on ionization seem to be approximately parallel with the changes of volume on forming the corresponding hydroxides; just as the heats of ionization are approximately parallel with the heats of formation of the hydroxides. This parallelism may indicate that the effective agency causing ionization or galvanic solution of a metal is the attraction of the metal for the oxygen or the hydrogen of water — most probably the oxygen.[4]

Although these regularities are fairly prominent on comparing

4. Richards, *Proc.* Am. Acad., *37*, 13 (1901).

the properties of similar elements in a natural group, exceptions are not hard to find on comparing very dissimilar substances. Reason for these irregularities may partly be found in the extremely complex mathematical relations which must obtain if the atom is really compressible; but probably, at least, a part of the exceptions may be traced to the expected simultaneous contraction of the solvent already predicted. That the solvent really often contracts is manifest from the fact that in some cases (notably the hydroxides of lithium, sodium, and barium, and the sulphates of zinc, cobalt, nickel and magnesium) the solution occupies less space than the water alone, from which it is made.[5] In this connection it is worth while to call attention to the well known fact that during the formation of eighteen grams of water from its ions in the neutralization of a strong acid by a strong base, an increase of volume of 20 millilitres occurs — an increase greater than the volume of the water formed.[6]

Although by no means all possible cases can now be studied, because of lack of data, there is good reason to believe that in all cases both the solvent and the dissolved substances change in volume under the readjustment of internal pressures of ionization; and the resultant effect is so complicated that it is impossible, at present, except in the most exaggerated cases, to determine the mode of the distribution of the change.

Nevertheless, since changes of volume actually occur on ionization, and since in the more marked cases this volume-change seems to correspond roughly to the known compressibilities of the substances, and to the free-energy change during the reaction, the theory of compressible atoms is supported. At least, even supposing that the explanation herein given is rejected, the theory is here able to call attention to an interesting series of facts concerning volume-change, which must receive an explanation before a complete interpretation of the nature of a dissolved electrolyte is obtained.

Another less direct relation of the theory of compressible atoms to electrochemistry is to be found in the effect of change of volume of reacting systems upon their specific heat. Thomsen pointed out long ago that a contraction in a reaction between aqueous solutions is usually accompanied by a loss of heat-capacity of the

5. Thomsen, "Thermochemische Untersuchungen." I. 45 (1882). MacGregor *Trans.* Roy. Soc. Canada, 1890, Sec. III, p. 19; 1891, Sec. III, p. 15; *Trans.* Nova Scotia Inst. Nat. Sc., 7, 368 (1890).

6. Ostwald, "Volum-Chem. Studien." *Pogg. Ann.* Erg. Bd., 8, 154 (1876).

reacting system; and it is possible to cite many other cases in which this is true. Probably, however, the cause of this loss is not so much the decrease in volume, as the irregular stress caused by the simultaneous presence of very different affinities. In terms of the hypothesis of compressible atoms:— atomic distortion seems to cause a diminution of heat capacity. As a kinetic conception, this interpretation is plausible.

The relation of this change of heat capacity to electrochemistry is very important. Recent study has made it appear highly probable that a change in heat capacity during a reaction is the chief, if not the only, reason why the total-energy change (or the heat of the reaction) is not equal to the electrical work which the reaction performs in a galvanic cell.[7] In colloquial language, the heat energy which is displaced, or forced out, by a diminution of heat-capacity, does not seem to be able to perform work. If this be true, change of heat capacity is responsible for the "bound energy" of a galvanic cell, and, therefore, according to Helmholtz's equation, for its change of potential with the temperature. If, further, the preceding conclusion based upon the theory of compressible atoms be also accepted, the fundamental cause of this temperature coefficient of the electromotive force is referred back to atomic compression and distortion, which diminish the possibility of heat-vibration in the compressible atom.

One essential condition of ionization has not yet been dwelt upon; namely, the relation of ionization to the quantity-dimension of electricity. Recent investigation has shown that Faraday's law is not merely an approximation, but is rather one of the most exact of the laws of nature.[8] If the atomic theory be accepted, one must therefore admit that each similar atom, on ionizing into a liquid, receives or releases *exactly* the same charge, which is a precise, simple multiple of a given unit. What now does this unit of charge signify? In other words, what are the essential attributes of electrical quantity, and what explanation for this exact and fundamental law can be found in the theory of compressible atoms?

To the electrochemist who has nothing to do with electrical capacity, the quantity-dimension of electricity is important merely as a number. He recognizes it only because it is proportional to

7. Richards, *Proc.* Am. Acad. *38*, 293 (1902). Van't Hoff, Drude's *Ann.* Boltzmann, Fest-Schrift, 233 (1904).

8. Richards and Heimrod, *Proc.* Am. Acad., *37*, 415 (1902); Richards and Stull, *ibid.*, *38*, 409 (1902).

equivalent weight of deposited metal, or to equivalent volume of evolved gas. Still more simply, it may be said to represent to him nothing but the number of atomic contacts which are made or broken in a given reaction. Therefore, the electrochemist, attempting to discover the relation of the compressible atom to galvanic deposition, naturally first seeks to imagine what would happen to a compressible atom on making or breaking a firmly united atomic contact with another atom.

Evidently, for each union with other atoms, a given atom would give and suffer a shock of impact or combination. The exact effect of this shock upon the atom itself cannot be determined; but if the atom is compressible throughout, many forms of vibration or temporary rhythmical distortion might be possible because of this shock. One of the most probable forms is perhaps a vortex motion; and it will be seen that this form lends itself best to further interpretation. If the internal substance of the atom were perfectly frictionless, such a vortex would continue to exist indefinitely, when once formed.

Let us imagine, then, that each collision of atomic combination starts or transfers a vortex or some other form of self-perpetuating shock.[9] Then the deposition of a given number of chemical equivalents will result in the transfer of a given number of shocks, or a given quantity of electricity, and Faraday's law is explained. In short, in order to conceive logically of this law, one need not ascribe weight or mass to the electron,— a permanent vortex will represent the needed unit as well as a ponderable particle. But only a compressible atom could hold or carry such an infinitesimal vortex, hence this hypothesis is dependent upon the hypothesis of compressible atoms.

This easy explanation of Faraday's law without a material conception of electricity leads one to inquire whether or not other relations of electricity might not likewise be satisfied by a vortical conception of the unit of electrical quantity. A complete study of the details of this possible explanation would be out of place, but a few of the electrical properties of substance may be mentioned

9. It is not important for this explanation that the disturbance should be precisely the wing-vortex usually meant by this word. Any kind of permanent twist or whirl might answer. No attempt is made in this paper to decide whether the difference between positive and negative consists simply in a respective deficiency and excess of these vortices, or in a difference between right and left-handed motion, which Professor A. E. Kennelly has suggested to me as possible.

in this connection. For example, the electrical conductivity of solids is in many cases what it would be expected to be, if their atoms were compressible. Atomic distortion would be expected to interfere with the ready transference of the vortices. The simpler the crystalline form, the less distorted would be the individual atoms, and the more easily would the vortices be received and transmitted from one atom to another. On the other hand, with irregular atoms, permanently distorted by chemical affinity, the uneven structure would receive and transmit the vortices less easily, and the potential energy of the mutual repulsion would be converted into heat. As a matter of fact, the two best electrical conductors among metals, silver and copper, crystallize in the regular system, and the poorest solid conductors among pure metals, bismuth, antimony and arsenic, are of less symmetrical crystalline structure. The non-metals which are all poor conductors, are still more noticeably complex in symmetry; and such non-conducting substances as bromine and iodine must be very much distorted in atomic shape, if their atoms are compressible, because these atoms must be much compressed on one side, by their firm union to form the diatomic molecules, and only slightly compressed on the other sides, by their feeble cohesion, indicated by great volatility. The relatively slight conductivity of alloys and compounds points in the same direction; for heterogeneity of atomic structure would imply irregular internal pressures, great atomic distortion, and hence poor conductivity. The considerable effect on conductivity of even slight impurity in a metal and the extremely low conductivity of substances like glass and cellulose are well known, and accord with this interpretation.

Again, it is easy to see how increased thermal energy, which, if atoms are compressible, must be supposed to exist as a simpler oscillation of a portion of the atomic centers, would interfere with the reception and transmission of this new vortex-motion, and hence to see why the conductivity of metals should decrease on raising the temperature. Moreover, one would expect the slightly distorted atoms, easily receiving the electrical vortex, should usually likewise transmit more rapidly the simpler oscillations of heat energy, which is a fact.

In applying the vortex idea to the statical and magnetic manifestations of electricity, one must imagine the vortex to cause stress in the surrounding wave-bearing medium, giving rise to the repulsion of similar vortices. Such a stress must be imagined whatever

conception one forms of the electron, and is at least as easily conceivable from a vortex as from a small particle of matter.

The explanation of the brilliant experiments of J.-J. Thomson and his pupils on the basis of the vortical electron is possible, if one admits, as Thomson is quite willing to do, the existence of electrical inertia independent of gravitational effect. In this case, the cathode ray is to be considered as a collection of disembodied vortices, which may only be driven through the wave-bearing medium under the stress of great difference of potential. Another alternative must be adopted if one doubts the somewhat complicated evidence concerning the relative masses of the cathode-corpuscle and the atom, and believes the two to be identical. In this case it is necessary to imagine that a single atom can receive many vortices under the peculiar circumstances attending the cathode discharge.

Other possible relations of the hypothesis of compressible atoms to electrochemistry and to the new and surprising facts of radioactivity might be pointed out, but these examples will serve the present purpose. The object of this paper has been to show that the hypothesis is a suggestive one, because it views well known phenomena from a new standpoint, and therefore may excite the imagination into devising new methods of experimental attack. The discovery of the probable relation of the change of heat-capacity to the temperature coefficient of a galvanic cell is among the new relations to which this hypothesis has already led.

The long continued illusion of phlogiston, supported by eminent minds not much over a century ago, is enough to show the danger of a one-sided scientific consciousness, and the familiar conception of inflexible atoms may also to a less degree lead the literal mind into an intellectual rut. Of course no claim is made that the hypothesis of compressible atoms represents truly the actual fact: indeed atoms, in any shape, are an imaginary conception which may have no counterpart in reality. Even if the thinker progresses no farther than to admit that, provided atoms exist, they *may be* elastic and compressible, he has broadened the train of his thought and enlarged the realm of his imagination.

It has been claimed by a few that any hypothesis is harmful; but some of the most brilliant of scientific workers have used them as a continual inspiration. Faraday, one of the greatest of pioneers, dreamed thousands of such scientific day-dreams. To him, these were nothing but a benefit; for although led on, by visions, he

knew well the difference between substance and shadow. He never confounded hypothesis with fact; and when new facts overthrew a favorite imagination, he would discard the latter gladly, rejoicing that it had led him to the discovery of new truth.

Discussion.

The Chairman, Prof. H. S. Carhart: I would like, myself, to call attention to the long paragraph in the middle of page 12, in which the writer of the paper is discussing the question of compressibility and atomic distortion as the cause of the diminution of heat capacity, wherein he draws the inference that this diminution of heat capacity may account for the well-known fact that the total electrical energy, or the heat reaction, is not equal to the electrical work which the reaction performs in the galvanic cell; or, as I prefer to say, the voltaic cell. The author then proceeds to draw the conclusion that the heat which is thus forced out, or displaced, by this diminution of the heat capacity, does not seem to be able to perform work. That statement would appear to be purely hypothetical, as no reason whatever is given for such statement.

Further, if I understand the position of the author, his theory accounts for the difference between the total energy-change in such a reaction, and the energy given out in the electric circuit only when the temperature-coefficient is negative. You will observe that he says that this heat which is forced out by the compressibility or distortion of the atoms, is not able to perform work. It would, therefore, tend of course to heat, or raise the temperature of, the voltaic cell. This is consistent only with the case in which the temperature coefficient of the cell is negative, not positive. The temperature of a voltaic cell, of which the temperature coefficient is positive, falls when the cell furnishes a current. In that case, the energy given out electrically is in excess of the heat of reaction, and this is sufficient to account for the fall of temperature; but the author's theory would require atomic expansion and increase of heat capacity. So, if this hypothesis is to account for the temperature-coefficient of the voltaic cell on the basis of the author's statement, it will answer only for a negative temperature-coefficient, and not for a positive temperature-coefficient.

Doctor Patterson: Is it not possible that expansion may take place in these cells that are exceptions?

Chairman: The author does not call attention, I think, to any case of atomic expansion in voltaic cells, but only to contraction.

On motion, the Section then adjourned.

Tuesday, September 13.

Joint Session of Section C and the American Electrochemical Society.

In the absence of Chairman Carhart, Dr. Wilder D. Bancroft was appointed to the chair, and Mr. S. S. Sadtler to act as secretary.

The following paper was then read by the author:

ELECTRICAL EXTRACTION OF NITROGEN FROM THE AIR.

BY J. SIGFRID EDSTRÖM.

One of the most important minerals ever discovered is the Chile saltpeter. The saltpeter earth "Caliche" is found in northern Chile in layers of from a half to four meters deep. It contains between 15 to 65 per cent nitrate of soda ($NaNO_3$) and is changed in a number of factories in Chile into the so-called "raw saltpeter," which contains about 95 per cent nitrate of soda, and is shipped in this form all over the world. The Chile saltpeter is chiefly used for manufacturing nitric acid and fertilizers. In the year 1901 the consumption of Chile saltpeter in Germany alone was 500,000 tons. Of this quantity 75 per cent were used for fertilizers, 20 per cent for the manufacture of nitric acid, 3 per cent for the manufacture of nitrate of potash, and 2 per cent for the manufacture of sulphuric acid.

The demand for Chile saltpeter is increasing and the consumption growing heavier every year in spite of the rapidly rising prices. We may well ask if the saltpeter mines in Chile are inexhaustible. Several investigations have been made as to the extent of the saltpeter deposits in Chile, and the reports vary from 30 to 125,000,000 tons. We will probably come very close to the truth if we calculate that 100,000,000 tons still exist. When answering the question how long the deposit in Chile will continue to last, we must take into consideration two factors which primarily affect the life of the mines. First, the consumption, and second, the possibility of finding new saltpeter mines or means of manufacturing substances of equal qualities.

If we assume that the export of Chile saltpeter will develop at the same rate in the future as it has during the last 10 years, we can easily calculate how long the supply of the present mines will last. Fig. 1 shows graphically the report of Chile saltpeter during the years from 1830 to 1900. The export during the year 1900 was 1 1/3 million tons, and the yearly average increase during the last 10 years about 50,000 tons. Basing the future con-

sumption on the figures given above, the saltpeter mines would be exhausted somewhere about 1940.

Many efforts have been made to discover new deposits, but so far without success. Another way of counteracting the shortage of Chile saltpeter has been to substitute other chemicals, such as sulphate of ammonia for fertilizers, but this material is not to be had in sufficient quantities.

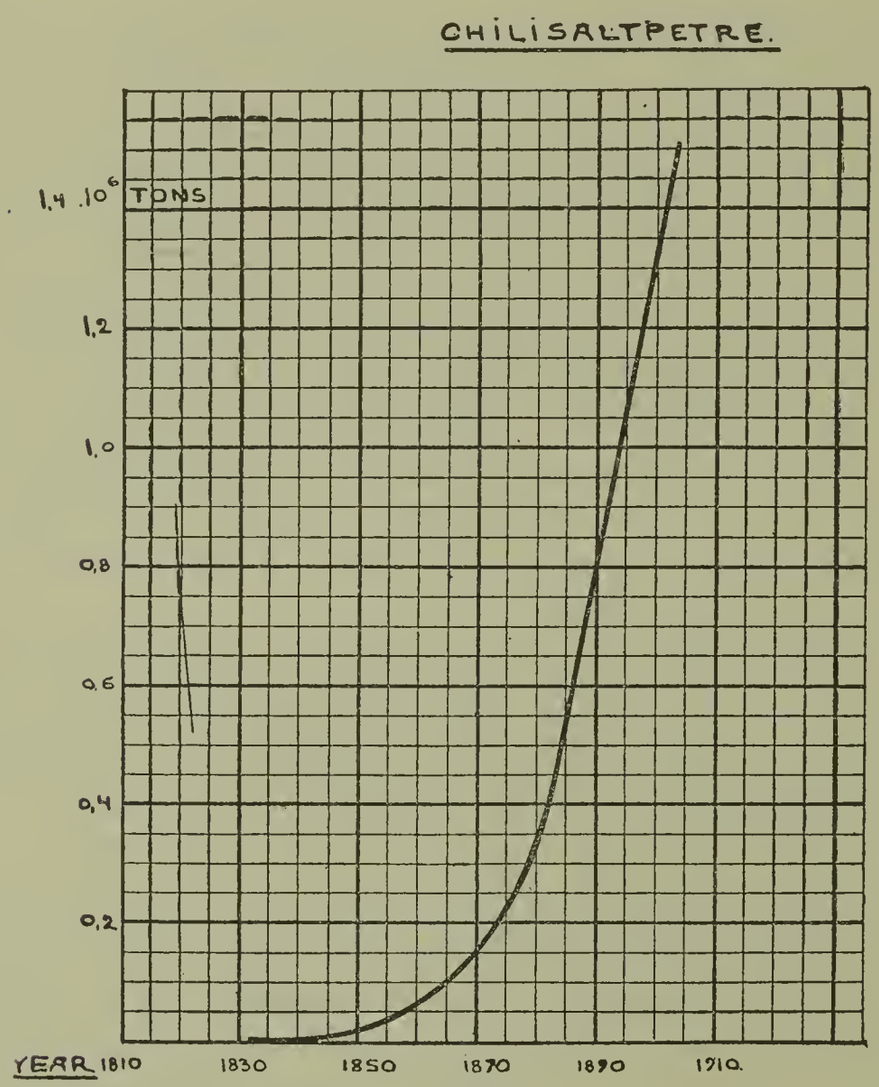


FIG. 1.

Some years ago experiments were made to produce the required nitrogen from the air by the application of bacteriology. The artificial production of an excess amount of bacteria in the earth and seeds tend to increase the power to absorb nitrogen from the air. The experiments have, however, not lead to any rational and economical application of this method.

Under these circumstances it is not to be wondered that in several ways other means of producing compounds of nitrogen have been sought. The nitrogen which is contained in the air

has been the source which has most naturally been turned to in seeking to produce a commercially useful article.

The Siemens & Halske Company, of Berlin, investigated a method invented by Dr. Frank for manufacturing cyanamide of calcium ($CaCN_2$). Originally carbide of calcium was heated and treated by a current of nitrogen. The nitrogen was received by carrying a current of air over glowing copper. The copper unites with the oxygen of the air and the nitrogen remains. Later, the same results were obtained by carrying the nitrogen over a heated mixture of chalk and carbon in the same proportion as used in making calcium-carbide.

The cyanamide of calcium has been tried as a fertilizer with good results. The method of Frank is as yet, however, only in its experimental state.

Most of the experiments for the manufacture of compounds of nitrogen are based on a compound with oxygen. Owing to the inert character of nitrogen it has been very difficult to bind and utilize the nitrogen of the air. As long ago as 100 years physical science knew, through the investigations of Priestley and Cavendish, that electric sparks through air caused the nitrogen and oxygen of the air to unite, and that nitric acid would be obtained as a product by this process. Toward the end of the last century this process was furthermore investigated by Wills, Plücker, Dewar, Lord Rayleigh and others, but it has been during the present century that investigations have pointed to a practical solution of the problem.

It was principally through the immense development of electricity that means have been provided for the solution of the problem. The first results from the experiments of oxidizing the nitrogen of the air were published by the Atmospheric Products Company, whose method was invented by Bradley and Lovejoy (*Electrical World and Engineer,* Aug. 2, 1902). The apparatus used in carrying out this method consisted chiefly of a solid drum or cylinder with a large number of platinum points placed inside the drum. Within the drum another cylinder is placed with points outwards. When the outer or inner drum is rotating the points come close to each other. The drums are connected to opposite sides of a high-tension direct-current system (8000 to 10,000 volts). When the distance between the points is small electric arcs are formed between the points. Through the motion of the drums

the arcs lengthen the break. At each arc under these circumstances naturally offers an exceedingly variable resistance, an inductive resistance is placed in series to regulate the current. Through the space between the two drums a current of air is sent, part of which is oxidized through the contact with the arcs. The fundamental idea of this invention is to obtain an electric arc of maximum length and minimum cross-section, in order to bring the largest possible volume of air into contact with the surface of the arcs. This determines the efficiency of the system, as the energy consumed in the arc is proportional to its volume. It is evident that this effort of subdividing the arc results in a device in which the multitude of arcing points required for large capacities forms an objectionable feature in practical application.

The efficiency of the Bradley and Lovejoy system has been said to be one ton of 70 per cent nitric acid per kilowatt and year. This corresponds to about 700 kilogrammes hundred per cent HNO_3. Any further developments of this system have not been published, so far as I know.

Another method has been proposed by de Kowalski and M. Moscicki. According to the publication in the *Bulletin* of the Société Internationale des Electriciens, 3d June, 1903, his method consists of exposing the air to an oscillating electric arc with a pressure of 50,000 volts and a frequency of several thousand periods per second. The method uses the well-known combination of self-induction and capacity. Its efficiency is said to be one kilogram if HNO_3 per 15 kw-hours, which corresponds to 580 kilogrammes HNO_3 per kilowatt and year. Also in this method the amount of energy needs to be largely split up, thus complicating the apparatus in order to get good efficiency, when applying large amounts of energy.

A new method for the solution of the problem was invented about one year and a half ago by Prof. C. Birkeland and Mr. S. Eyde of Christiania. As far as now can be seen this method should give comparatively good results.

Prof. Birkeland and Mr. Eyde based their arrangements on the well-known fact that the electric current in the arc and with it the arc itself, can be deflected by a magnetic field, the deflection being at right angle to the lines of force.

Based on this fact, Prof. Birkeland and Mr. Eyde proposed a large number of arrangements, of which I will describe the one

which seems to give the best results. In Fig. 2 are shown two electrodes, E and E_1, which are connected to the poles of the electric generator G. The points of the electrodes are at such a distance that the pressure of the generator can maintain an arc between the electrodes. If a strong magnetic field is applied near the electrodes and at right angles to the direction of the electrodes, as shown in Fig. 2, the arc between the electrodes will momentarily be carried upward or downward, the direction of the current being for the moment from right to left or opposite.

For several reasons (one of which being the loss of pressure in the resistance L connected in the circuit) the pressure will fall between the electrodes at the moment the arc is formed.

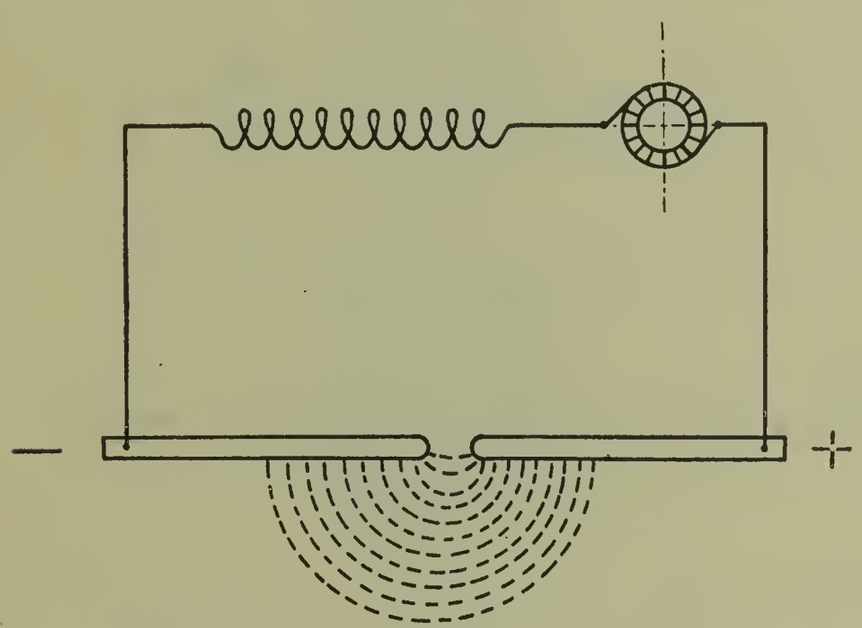


FIG. 2.

The arc will be carried outward by the magnetic field and grow longer as indicated by the dotted lines. Its resistance, consequently, rapidly increases until the pressure between the points is sufficiently high again to cause another arc between the electrodes. This arc having a lower pressure than the first one, the current will all pass through it, and the first one is extinguished. The speed of the arc is so rapid, however, and the formation of the new arc so instantaneous, that the arc can be formed several thousand times a second. In the practical form of the ovens only some hundred arcs per second are used. These arcs are formed, carried outward and extinguished so rapidly that to the eye they appear as a disc of arcs.

If the magnetic field is excited by a direct current, and the

generator delivers direct current for the arc, a continual series of arcs will be formed. These arcs move radially with a speed corresponding to the strength of the magnetic field. The striking points of the arc along the surface of the electrodes are also moving away from the points at the same speed. Thus the phenomena appear to the eye like a disc of arcs with the shape of almost a complete semi-circle. The movement of the arc near the electrodes is usually more rapid at the negative than at the positive electrodes, shifting the center of the circular disc somewhat to one side of a line joining the electrodes. If the magnetic field is excited by alternating current and the arc is fed by direct current, the arcs will vibrate between opposite sides of the elec-

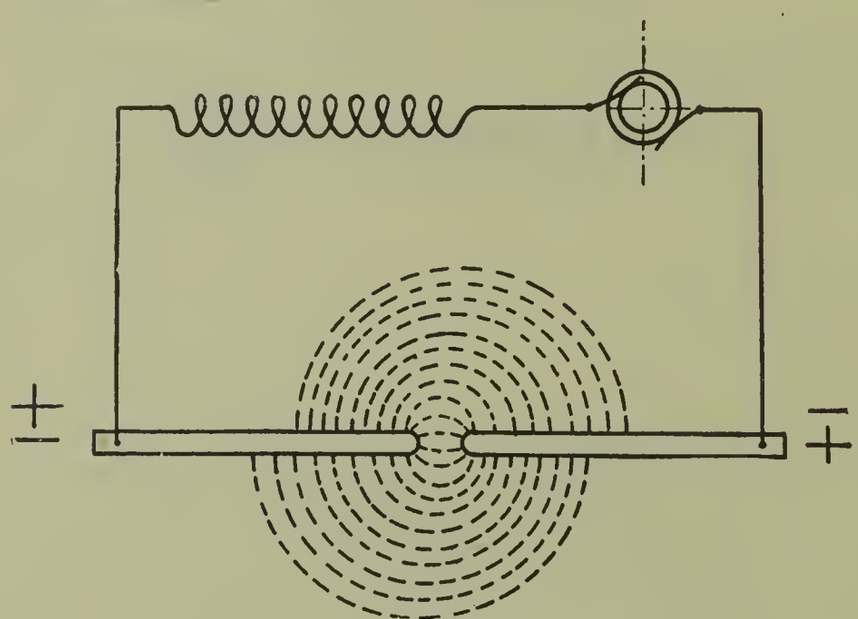


Fig. 3.

trodes. This will also be the case if the arc is fed by alternating current and the magnetic field by direct current, in which case the phenomena will appear as indicated in Fig. 3. It is principally this arrangement which has been used.

Fig. 4 shows the electric oven complete in a vertical section at right angles to the electrodes. The air that is to pass the oven is forced through the channels *A* and from them into the arc-chambers of the oven *B*, around and in the neighborhood of the electrodes *E*. Having passed this space from the center, and coming into the most intimate contact with the disc of arcs, the air passes out into the channel *C*, and leaves the oven mixed with a certain percentage of oxidized nitrogen.

If we look closer at this oven and the principles according to

which it works, we may easily discern the chief difference between this invention and the methods described before. The difference will be most strongly marked by quantitative results. While, with Bradley and Lovejoy and de Kowalski's methods, the energy in every arc must be lowered to the least possible in order to obtain an economical system, the method of Birkeland offers no objection to employing large amounts of energy in the disc of arcs. On the other hand experiments have proved that the economical efficiency increases with the amount of energy employed at the electrodes.

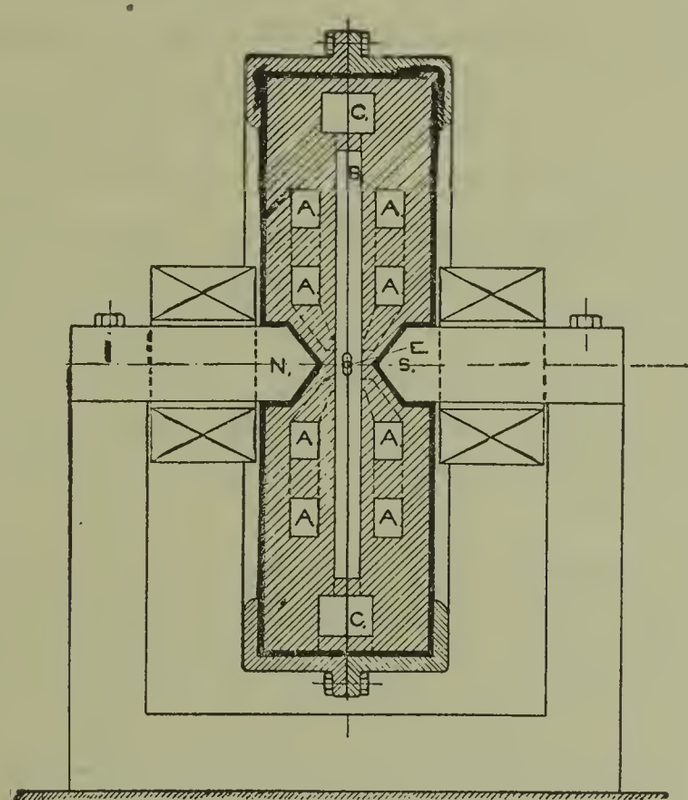


FIG. 4.

One of the ovens, which is still in operation, has consumed from 75 to 200 kilowatts in the disc of arcs between one single pair of electrodes, and lately an oven with a disc of arcs for 500 kilowatts has been built. The 200-kw oven has been fed with alternating current of 50 cycles frequency and 5000 volts pressure. From this will easily be seen that the amount of energy employed, and the class of current in the arc, can hardly be compared with the current that may be used by other methods.

In spite of the large amount of current the electrodes in Birkeland's oven have up to the present been used without interruption for several hundred hours. Owing to the fact that the striking points of the arc move along the electrodes, the destructive in-

fluence of the arc is inconsiderable. The electrodes can, for this reason, be made of very cheap material, such as copper or iron, and have such dimensions that they can easily be cooled by means of air or water, keeping their temperature within reasonable limits.

The oven of Birkeland and Eyde is consequently a very simple, strong and easily operated piece of apparatus, even when working with a large amount of energy. Electric current from any ordinary standard machinery can be used for its operation.

In the oven of Birkeland and Eyde, which was built about a year and a half ago, a small amount of energy was used in the disc of arcs only seven to ten kilowatts. The efficiency of this apparatus was at first only 400 kilogrammes HNO_3 per kilowatt and year. The next ovens were constructed for an increased consumption of energy and have now through continual improvements reached an efficiency of 900 kilogrammes HNO_3 per kilowatt and year. The energy referred to is the amount of energy in the disc of arcs itself.

This result has, of course, been gained after numerous difficulties and with many obstacles to overcome. I will not enter into the details of this work, but will only mention some of the factors that have been considered in connection with the improvement of the oven as follows:

The degree of moisture in the impressed air, its temperature, its amount of oxygen, its amount of air impressed per kw-hour, the different amounts of electric current used, the voltage of the electric current, the frequency, the ovens arranged in series and parallel electrically as well as with regard to the impressed gases, the strength of the magnetic field, the insulation of the oven to prevent the loss of heat, the introduction of various contact substances.

The air coming from the oven contains about 2 or 3 per cent of nitric oxide (NO). In order to be utilized it must be transformed into nitrogen peroxide (NO_2). This is done in a reaction tank of thin sheet iron enamelled on its inner side.

From the reaction tank the gases go through an exhauster of clay, where they come into contact with drips of thin nitric acid. From here the gases pass on through the absorption system, consisting of four towers for water and one tower for a solution of caustic soda. In each tower the fluid is sent through the tower several times. The strongest acid runs always through tower No. 1, where the gases first pass, the next strongest through tower No. 2,

and the weakest through tower No. 4. When the desired concentration is reached in tower No. 1 the acid is removed. The acid from tower No. 2 is then put into No. 1, from tower No. 3 into No. 2, from No. 4 into No. 3. Through tower No. 4 new water is passed. The process thus works according to the counter-current principle. The alkali tower contains, as previously noted, a solution of caustic soda. The gases from No. 4 pass through this tower. The remainder of the gases is absorbed here, and a mixture of nitrate and nitrite of soda is formed. From this pure nitrite of soda is manufactured.

The acid taken from tower No. 1 is either concentrated by use of Valentiner apparatus and shipped, or is turned into nitrate of calcium or nitrate of potassium (potash).

The Birkeland process has been put into actual operation, and compounds of nitrogen are being manufactured. It is to be hoped that the process will prove economical, and thus one of the greatest needs of the present time — cheap nitrogen in bound forms — will be introduced on the market.

The need of fertilizers is unlimited. Some years ago, when calcium-carbide was invented, numerous factories were built, and a great boom was given to the electrical industry. The market, however, proved too small, and the enterprise has languished. This can never occur with respect to the nitrogen industry, as the market is unlimited. Thus, if the industry is pushed forward, the electrical industry will benefit immensely. Moreover, all sources of energy will increase in value; waterfalls, situated in uninhabited parts of the earth, will be utilized, and great central stations in cities will, in many cases, obtain a profitable load now lacking. The immense waterpowers being all utilized, power will become cheap, which again will benefit industry in general.

Thus, if the process proves to be an economical success, the entire world of agriculture and industry will profit — and the process thereby will be a benefit to all mankind.

Discussion.

Prof. C. F. Burgess: These figures give 900 kilograms of nitric acid per kilowatt year, making it appear, therefore, that this is certainly a very valuable process. It appears that the efficiency is considerably higher than that claimed by the Niagara Falls process. But to interpret these figures correctly, the strength of the nitric acid should be given. I would like to hear what strength of nitric acid is to be obtained from this process.

Mr. Edström: It is 100 per cent nitric acid. One maker has attained a still higher efficiency, 950 kilograms per kilowatt-year, but I have given the intermediate figures.

Professor Burgess: If the 900 kilograms represent 100 per cent nitric acid, that would mean, at the present market prices, something like $90 worth of acid for one kilowatt year, which would be a very profitable process if the power is the chief item which would have to be considered in the cost of operation.

Mr. Edström: Yes; but of course there would be many losses in the process. I have shown the amount of energy consumed, and all the other figures are based on that consumption; but there is a loss afterward, by leakage in the pipes, or in the coil.

Professor Burgess: Then this figure does not include those losses?

Mr. Edström: It includes the energy in the arc itself.

Dr. E. F. Roeber: I understand your arc moves in a plane. You light it by direct current and use a magnetic field, produced by a single phase alternating current, for deviating the arc. If, however, you excite the arc by direct current and use a revolving magnetic field (such as produced by the primary of an induction motor) to divert the arc, you would cause the plane in which the arc plays to revolve itself; you will no longer have a disc of arcs, but rather a globe of arcs; this means that a greater quantity of air would be acted upon by the arcs. Possibly this might increase the efficiency of the process. Did you make any experiments in this direction?

Mr. Edström: In reply to Doctor Roeber, I beg to say that, as far as I know, Professor Birkeland has not made any experiments in the line indicated. I think that the apparatus built on this principle would, however, be very difficult to design and construct. The ovens are very heavy, the latest one built weighing some seven tons. However, I will call Professor Birkeland's attention to the new idea brought forth by Doctor Roeber and thank him for the suggestion.

The following paper was then read by the author, who resigned the chair to Prof. C. F. Burgess:

THE CHEMISTRY OF ELECTROPLATING.

BY PROF. WILDER D. BANCROFT, *Cornell University.*
Delegate of the American Electrochemical Society.

Although some results have been obtained by Mylius, Foerster, Glaser, Burgess and others, a glance at the recent text-books on electrochemistry will show how far we still are from any consistent theory of electroplating. The reason for this is to be found in our neglect of the chemistry involved. The electric current is merely one agent for bringing about certain chemical reactions; but this is often overlooked and many of us consider a decomposition by means of electricity as much more mysterious than a decomposition by heat, for instance. I hope to show that a study of chemical reactions and chemical analogies will at least give us the outlines of a theory of electroplating.

When we speak of a good metallic deposit we may mean good from the point of view of the analyst, the refiner, or the plater. The analyst must have a deposit of pure metal in a weighable form but that is all. The refiner must have a coherent deposit of pure metal, except in the case of silver. Neither the analyst nor the refiner cares about the smoothness of the deposit, so long as no trees are formed. The plater must have an adherent smooth deposit which will burnish to an apparently amorphous surface. In the preliminary discussion we will rule out the plater and will call a deposit good when it is pure and coherent. Afterwards we can consider the further problem of the production of a very fine-grained deposit. Since there are very few data for anything except aqueous solutions, we will consider these only, though the general principles are equally applicable to all solvents.

When working with moderate current densities a bad deposit is practically always due to the precipitation of a non-metallic solid with the metal. When one of the single salts in the bath is sparingly soluble, as with the cyanides, this salt may precipitate. In most cases, however, the trouble is due to the presence in the deposit of oxygen either as oxide, hydroxide or basic salt. Whatever

will dissolve the salt readily under the conditions of the experiment will prevent its deposition, by definition, and should therefore improve the quality of the deposit. This has been recognized for zinc by Mylius and Fromm[1] and by Foerster and Gunther.[2] It has been put in a more general form by Glaser.[3]

I have made a list of the more important additions recommended in the refining, analysis, or plating of zinc, nickel, lead, tin, copper and silver. These are given in Table I.

TABLE I.

Zinc	*Tin*
Sulphuric acid	Sulphuric acid
Potash	Potash
Ammonium chloride	Sodium pyrophosphate
Ammonium sulphate	Potassium carbonate
Aluminum sulphate	Acid potassium tartrate
Potassium cyanide	Potassium cyanide
Acid potassium oxalate.	

Nickel	*Copper*
Sulphuric acid	Sulphuric acid
Ammonia	Ammonia
Ammonium salts	Alkaline tartrate
Potassium cyanide	Ammonium oxalate
Sodium bicarbonate	Potassium cyanide
Sodium bisulphite	Sodium bisulphite

Lead	*Silver*
Acetic acid	Nitric acid
Potash	Ammonia
Fluosilicic acid	Potassium cyanide
Sodium nitrate	Potassium iodide

All the substances under zinc dissolve zinc hydroxide. The first four under nickel dissolve nickel hydroxide; the sodium bicarbonate probably serves to keep the acidity constant; while the sodium bisulphite occurs only in solutions containing free ammonia. All the substances under lead dissolve lead hydroxide. Stannous and

1. *Zeit. Anorg. Chem.* *9*, 144 (1895).
2. *Zeit. Elektrochemie*, *5*, 16 (1898); *6*, 301 (1899).
3. *Ibid.* *7*, 365, 381 (1900).

stannic acids are soluble in sulphuric acid, in potash, and in a so-called sodium pyrophosphate solution; potassium carbonate is added only to neutralize an excess of free acid in stannous chloride solutions; while the cyanide and tartrate seem to be of very little value, unless perhaps at the anode. Under copper everything dissolves the hydroxide except sodium bisulphite and this is added to cyanide solutions to prevent loss of cyanogen when the copper changes from the cupric to the cuprous form. All four substances under silver dissolve freshly-precipitated oxide; in addition ammonia dissolves silver chloride while silver cyanide and silver iodide are soluble in potassium cyanide and potassium iodide respectively.

It is thus clear that there is a simple rational basis for many of the solutions in actual use. It must be kept in mind, however, that the rate of solution is more important than the actual solubility. Thus it is not easy to get a good deposit from an alkaline zincate solution at 20° whereas it is a comparatively simple thing to do this at 40° because the caustic soda reacts with zinc oxide or hydroxide much more rapidly at this temperature. It does not follow from this that a higher temperature would necessarily be even better. At 90° the action of caustic soda on metallic zinc becomes an important factor. With copper sulphate solutions rise of temperature means increased formation of cuprous sulphate and this must be taken into account. In each of these cases a study of the chemical reactions shows the cause of the difficulty.

While there is much evidence in favor of Glaser's first generalization, that a metallic deposit is improved by adding to the solution substances which will dissolve the oxide, hydroxide or basic salt, there are only a few scattered experiments which can be cited in favor of Glaser's second generalization that reducing agents improve the quality of the deposit. Glaser[4] observed that addition of pyrogallol or hydroquinone to a lead bath improved the deposit of electrolytic lead. Engels[5] states that the addition of hydroxylamine makes it possible to use higher current densities in the analysis of copper. It is believed that tin salts in solution improve the quality of a copper deposit[6] and it is known that ferrous salts are not disadvantageous. Good deposits of many metals are obtained from cyanide solutions and part of the effect, though certainly not the

4. *Zeit. Elektrochemie*, 7, 381 (1900). *Cf.*, Elbs and Rixon. *Ibid.* 9, 267 (1903).
5. Smith. "*Electrochemical Analysis*," 62.
6. Borchers. "*Elektrometallurgie*," 193.

whole of it, may be due to the fact that potassium cyanide is a reducing agent. It is also possible that the merits of a tartrate solution may be due in part to the formation of reducing agents by oxidation at the anode.[7] In some experiments made at Cornell we have found that hydrazine improves the electrodeposition of cobalt and that resorcine has a slight favorable effect with zinc but apparently not with tin. The negative result in this last case may be due to the reducing power of the tin solutions. These instances will suffice to show that we do not yet know definitely how much influence a reducing agent has or how it varies with varying conditions. Since none of the reducing agents in question will reduce the oxide to metal, it seems very probable that the effect of the reducing agent may merely be to prevent oxidation by dissolved oxygen. If so, the effect should disappear in a vacuum or in an atmosphere of nitrogen. It has not yet been possible to try this experiment.

We have next to consider the effect of higher current densities. When solutions are not stirred we soon reach a point at which an ever-increasing current density causes a bad deposit. This change in the quality of the deposit is always accompanied by an increased evolution of hydrogen and it is usually believed that the evolution of the hydrogen is the cause of the deposit going bad. This cannot be the whole truth because hydrogen is evolved freely during electrolytic analyses and yet the deposit remains good. Further, the so-called critical current density varies enormously with the size, shape and distance apart of the electrodes, and also with the size and shape of the containing vessel, so that the data obtained by any one man usually cannot be duplicated by others. The most important factor is the rate of stirring. If we rotate a smooth copper, zinc or nickel cathode with sufficient speed it is by no means certain that there is any current density at which the deposit goes bad. With tin there does seem to be a limiting density but this is very possibly due to the formation of stannic salts in solution. It is intended to study this question in detail.

When a deposit becomes sandy or changes to a black powder, the polarization shows that there has always been the formation of a dilute solution at the cathode. In most cases this leads to the precipitation of an oxide or basic salt with the usual disastrous results.

7. Luther. *Zeit. Elektrochemie*, 8, 647 (1902); Schilow. *Zeit. Phys. Chem.* 42, 646 (1903).

It is still an open question whether this is always the case. Foerster and Seidel[8] say that sandy deposits of copper are not due to the presence of oxide. If this statement is correct, we shall be forced to the assumption that the badness of the deposit is due to the pulsating or intermittent precipitation of hydrogen as a result of the intermittent formation of a surface film impoverished as to metal. This explanation does not appeal to me personally and I prefer to believe for the present in the oxide formation even if I have to account for the apparent absence of hydrogen by assuming a reduction to metal after the harm has been done.

Hydrogen may easily be indirectly the cause of a bad deposit. If hydrogen adheres as bubbles to the cathode, the deposition of the metal will become uneven and we shall have conditions favorable for treeing. A trouble of this sort can be cured chemically by adding an oxidizing agent to remove the hydrogen. It is known that copper solutions containing nitric acid will stand much higher current densities than will those acidified with sulphuric acid. It is clear that the prevention of hydrogen by means of an oxidizing agent may lead to the oxidation of the metal in which case we are out of the frying-pan into the fire. Foerster and Gunther[9] had difficulties with hydrogen bubbles during the precipitation of zinc. They show that such oxidizing agents as chlorine and ammonium persulphate prevent the appearance of hydrogen without causing the formation of zinc oxide. Such oxidizing agents as hydrogen peroxide and ammonium nitrate prevent hydrogen evolution but were worthless because they oxidized the zinc.

An oxidizing agent could probably be used to prevent occlusion of hydrogen by nickel, for instance. It is quite likely that the disadvantages would outweigh the advantages. In that case it would be better to approximate the same result by varying other conditions. The favorable conditions would be: a concentrated solution to ensure a good deposit; a high temperature to lower the obsorption coefficient; a nearly neutral solution to increase the decomposition voltage of hydrogen; and a high current density to give a fine-grained metal. For any given rate of stirring we should expect a limiting current density beyond which deterioration would occur. With increasing current density we get a finer deposit but there is also an increasing tendency to precipitate hydrogen and it is necessary to strike a balance between these two. All these conditions

8. *Zeit. Anorg. Chem.* *14*, 125 (1897).
9. *Zeit. Elektrochemie*, *5*, 22 (1898).

have been found experimentally for nickel by D. H. Browne[10] with the one exception that he finds a large addition of sodium chloride advantageous.[11] The reason for this is not clear.

Having considered the conditions for getting a good deposit from the refiner's point of view, we can now take up the question from the point of view of the plater. The problem is now as to the conditions under which the deposit is composed of very small, microscopic crystals.

When we precipitate a salt by chemical means we get larger crystals, the slower the precipitation and the higher the temperature. We should therefore expect that an electrolytic deposit will be coarser the lower the current density and the higher the temperature, provided all other conditions are held constant. The conclusion as to the current density is confirmed by all experiments. The case of the temperature change is a little more complicated because we may have hydrolysis and increasing acidity or alkalinity; we may have increased solvent action; and we may have a displacement of equilibrium as with copper sulphate. The effects due to these changes will of course superimpose themselves on the pure temperature effect and mask or even reverse it. In some experiments made in my laboratory Mr. Snowdon found that the deposit from an acidified copper sulphate solution became coarser as the temperature was raised from 20° to 40° and to 70°C. A similar result was obtained with a strongly acid zinc sulphate solution and with a lead bath. With nickel ammonium sulphate solution the effect of temperature on the crystalline structure of the deposit was too small to be detected. With a zinc sulphate solution which was only slightly acid, the deposit was more finely-grained at 40° than at 70°; but the deposit at 20° was coarser than either of the others. I suspect that at 20° the slight acidity had no appreciable effect on the deposit while it became an important factor at 40°. This hypothesis is confirmed by the other experiment in which a more acid solution behaved normally.

For a given current density, temperature and salt solution, we should expect a coarser-grained deposit the more concentrated the solution. This has been found to be the case in experiments with zinc sulphate and sodium zincate solutions. Since the potential difference between the metal and the solution is less the more con-

10. *Electrochemical Industry*, *1*, 348 (1903).
11. Cf. Pfanhauser, *Zeit. Elektrochemie*, 8, 594 (1902).

centrated the solution, it seems probable that this is an important factor when we change from one solution to another. Other conditions being the same we shall get the smallest crystals, the greater the potential difference between the metal and the solution. This is the recognized explanation for the excellent character of the deposits from cyanide solutions.

A natural corollary from this last is that the deposit will be more finely crystalline, the greater the solvent action of the solution. This accounts for the small crystals that are obtained from an acid copper sulphate solution or from one containing nitric acid. This conclusion of course holds only within the limits for which we get a good deposit. The converse of this would be that reducing agents should increase the size of the crystals. Mr. Snowdon has found that addition of formaldehyde to a copper or a zinc solution does make the deposited metal more coarsely crystalline. Resorcine has a similar effect with zinc. It will be difficult to get conclusive evidence on this point because many reducing agents form complex salts and the effect due to this may easily overbalance the other. If the reducing agent acts only to remove dissolved gases, its effect on the size of the crystals would probably be negligible.

The addition of glue or similar substances to a solution tends to make precipitates come down in a colloidal form. Following out this analogy we should expect to find that addition of glue or similar substances to an electrolytic bath would decrease the size of the metal crystals, the limiting concentration being that at which the added substance causes a bad deposit owing to its chemical properties. It is known that the success of the Betts process for refining lead is due in part to the action of glue in preventing trees. We have found that the addition of ten grams of glue per liter of acidified copper sulphate solution improves the quality of the deposit from the plater's point of view.

One final point is of importance to the plater, the adhesion of the deposit. It has been suggested that an adherent plating deposit can be obtained only when the two metals can combine to form compounds or solid solutions.[12] This has also been denied.[13] While I have not yet made any experiments myself, I feel certain that Burgess is right and that this is purely a question of chemistry. The surface between two metals is a thin weld and it must show the

12. Kahlenberg. *Electrochemical Industry, 1,* 201 (1903).
13. Burgess. *Ibid.* 204.

same strength no matter how it has been made. In other words the adhesion of an ideally-made electrolytic deposit will approach that of a casting having the same size of crystals. Presence of grease, of air-bubbles, or of occluded mother liquor will impair the contact and weaken the joint. If the metal be deposited in a state of strain, the break will come at the weakest point. These are matters of general knowledge in making welds or castings and they are just as much first principles in electrolytic work. No one seems to have been struck by the absurdity of the statement, to be found in most books on plating, that nickel cannot be plated on nickel because it will not adhere. If this were true it would not be possible to deposit more than an infinitesimally thin film of nickel electrolytically. While it requires a higher voltage to deposit nickel than copper, nickel does not precipitate copper to any appreciable extent when immersed in a copper sulphate solution. The nickel becomes passive and is probably covered with a thin film of oxide. What people mean is that an "active" nickel containing hydrogen will not adhere to a "passive" nickel. There is nothing surprising or mysterious about this.

The alleged rusting of iron, when plated with nickel in a chloride instead of a sulphate solution, if really true, is purely a chemical phenomenon and rests on the different behavior of occluded chloride and sulphate solutions. If the distinction is a real one, special experiments would soon show whether the freedom from rust in sulphate solutions is due to the iron becoming passive or to the formation of an insoluble basic salt.

The general results of this paper are:

1. A bad deposit is always due to the precipitation with the metal of some salt or non-metal.

2. Addition to the solution of anything which will dissolve this salt or non-metal will tend to prevent its precipitation and to improve the quality of the deposit.

3. Any beneficial action of a reducing agent is probably due to the removal from the solution of dissolved oxygen.

4. A fine-grained deposit is favored by high current density and potential difference, by acidity and alkalinity, by low temperature, and by colloids.

5. Solutions containing oxidizing agents appear to yield small crystals while larger crystals are obtained from solutions containing reducing agents.

6. The adherence of deposits rests on the adhesion of the two metals.

The discussion has been incomplete. The formation of "trees" has only been touched upon and the question of "bright" deposits has not been raised. All of the generalizations rest on insufficient evidence. On the other hand, the consideration of the chemistry of electroplating has given us a working hypothesis which can be tested experimentally.

DISCUSSION.

Mr. Edward F. Kerns presented the following communication on the subject from Prof. Anson G. Betts:

Professor Bancroft's paper, in my opinion, does not bring us any nearer a solution of the important question raised. It seems to me that there can be no scientific question concerning which it is more unsafe to build up theories without experimental verification of the data available. The reason for this is that experimental results and hypotheses are so conflicting.

I am not familiar with most of the references Professor Bancroft cites, but have repeated all the experiments in the articles by L. Glaser, which are referred to, and a great many others beside, in lead deposition. I have been entirely unable to verify this author's result claimed of a solid lead deposit.

I will give a few quotations from these articles, and think if Professor Bancroft had studied them he would not have based any theories on them.

"A solution of 40 grams of nitrate of lead and 10 grams $NaNO_3$ in 100 cu cm H_2O was treated under boiling with freshly precipitated hydroxide of lead. The solution, filtered while hot, still showed a slightly acid reaction. When cooling off, a part of the lead is again deposited as basic salt. A plain sponge formation is at once produced on the cathode. *It is thus proven that the solution has lost its property of depositing solid lead through treatment with hydrate.*"

Also he says, speaking of the first experiment he describes:

After the cathode lead had become about 2 mm thick, the plate was taken out and it was found that especially the upper part of the plate did not consist of pure lead, *but was intermixed with oxide although it was not yet possible to recognize a sponge formation.*"

His experiment 4 repeated with a current density of .6 ampere per sq. dm, gave a deposit consisting of a loose mass of crystals. In fact the deposits obtained by repeating these three experiments were practically the same in crystallization, the intermixed hydroxide exerting little or no influence on the structure of the lead crystals.

In repeating Glaser's experiments with the addition of ammonium persulphate to the electrolyte, which he recommends, I found that lead sulphate was formed on the cathodes, by the reaction between persulphuric acid and metallic lead. The white lead sulphate could be seen all through the deposit, but there was no difference in structure to be observed from

that obtained from the same solutions without the addition of the persulphate.

Professor Bancroft refers to "Glaser's second generalization that reducing agents improves the quality of the deposit." There is no such generalization to be found in these articles. The statement to which Professor Bancroft refers is probably the following:

"The addition of stuffs which can dissolve the basic salts, such as persulphate of ammonium in small quantities, likewise the development of hypochlorous acid in the bath, greatly increase the solidity of the precipitation. Additions of pyrogallol, hydrochinon, etc., have the same action." As persulphate of ammonium and hypochlorous acid are oxidizing agents, and hydrochinon and pyrogallol are reducing agents, it is difficult for me to see the derivation of the generalization.

Some of the general results of Professor Bancroft's paper are:

1. "A bad deposit is always due to the precipitation with the metal of some salt or nonmetal."

a). We have seen that the codeposition of lead hydrate and lead sulphate does not materially affect the character of a lead deposit, at least under some conditions, which are common enough.

b). Traces of cadmium added to a zinc sulphate solution cause a deposit of zinc which is perfectly solid and dense to immediately become spongy. Also lead electrolytes which contain considerable antimony and arsenic give a slimy deposit. In these cases we have the coprecipitation of neither a salt nor a nonmetal, but a foreign metal. The actual facts seem to me to be that the codeposition of some salt or nonmetal is detrimental merely to the extent that the foreign material occupies space that should be filled with metal, in order to get a solid deposit, but that the deposition of foreign metal particles, which will not alloy with the principal metal, at the moment of formation, is a very serious matter.

Result 2 is Result 1 stated conversely.

4. "A fine-grained deposit is favored by high curve density and potential difference, by acidity and alkalinity, by low temperatures and by colloids."

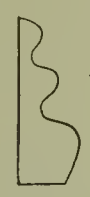
It was always my opinion that a low current-density rather favors a fine-grained deposit, and in the absence of any experimental data to prove the contrary, I do not see any reason why I am not as apt to be right as Professor Bancroft. With regard to temperature, it has been stated that with nickel at least a temperature of 70 deg. C. is better than a lower temperature. It may be that colloids are useful in improving the texture of a deposit, but I have made some attempts to get solid deposits with this means and been unable to.

5. "Solutions containing oxidizing agents appear to yield small crystals, while large crystals are obtained from solutions containing reducing agents." From a lead fluosilicate solution at least, in the absence of reducing agents, splendid large crystals are obtained, while with the addition of gelatine to the solution, the deposit is perfectly solid and noncrystalline.

I should like to suggest a few ideas on this subject. We can recognize two distinct causes for the failure of an electro-deposit. A deposit may either fail from being slimy, grading off into being soft, unsound and weak. I believe this is due to the codeposition of foreign *conducting* par-

ticles, in general caused by the presence in the solution of a small quantity of some metal of less chemical affinity than the metal being deposited. The foreign metal is precipitated in the minutest particles all over the surface, and if it comes down in too large quantity, or its affinity for the main metal is so weak that it is not immediately absorbed into an alloy, the same phenomenon takes place on an atomic scale that takes place on a visual scale when copper, for example, is being deposited and particles of slime are floating in the electrolyte. A particle of anode slime attaches itself to the cathode and very soon causes the formation of an insecurely attached lump of solid metal. The lumps are usually very easily knocked off and a particle of slime is almost invariably found underneath. A slimy metal must consist of such lumps on an infinitesimal scale.

The other cause of failure is the growth of a deposit toward the anode; the more elevated a particular point is from the cathode surface, the more rapid its growth.



Consider a rough electrodeposit as shown in section in the sketch. From the deposition of metal the solution near the cathode is lower in metal percentage than the main mass of the electrolyte, as is shown by the rising column of electrolyte at the cathode. In the cavities of the deposit this change of concentration has gone farther than on the point of a projection. We have in fact here a concentration cell, of which these two points are the electrodes and the cavity is immersed in a weaker solution than the projection. If there is no e.m.f. of this concentration cell, the deposit will grow equally, and the projections and cavities will be graudually smoothed out. If the concentration e.m.f. is in the usual direction, that is, the metal has a higher e.m.f. of solution in the weaker solution, metal will deposit faster on a projection than it will in a cavity, and we will have a "tree." If the e.m.f. is in the other direction, deposition will proceed faster in a cavity than on a projection, and the deposit will actually grow smooth, or if started on a smooth surface will remain absolutely smooth, and will have a polish. This result is rarely reached in practice, and the best we can usually do is to find a solution in which the e.m.f of the concentration cell is practically zero.

In depositing antimony from a solution of antimony trichloride, in which ferric chloride was continually generated in small quantities, I obtained a deposit that was as smooth and shiny as glass. In this case the ferric chloride in the solution performed the function of continually cutting off projections as fast as started. By the time the iron salt had reached an incipient cavity, it had passed and already reacted with the antimony of a neighboring projection, so that the rate of reaction was less the less the particular point was in the current of solution. The amount of ferric chloride used was from one-tenth to one-fifth the amount necessary to redissolve all the antimony deposited.

Dissolved oxygen in a bath would, no doubt, have the same function

were it not for the fact that the reaction between oxygen, an acid and a metal is infinitely slower than between ferric chloride and antimony.

In depositing silver from a nitrate solution, the deposit consists of more or less loose crystals, and projections are formed. From the cyanide solution the deposit is dense and solid. The reason appears to be that with the cyanide solution the e.m.f. of the minute concentration cells that must exist at the cathode is much smaller than with the nitrate solution.

In an acid copper-sulphate electrolyte we have present both cupric sulphate and cuprous sulphate. It is probable that in the cavities of the deposit more cuprous sulphate is present than near the projections, and it is also probable that the e.m.f. of solution of copper is less the more cuprous sulphate there is in the solution, which would account for the lower e.m.f. of the concentration cells and the solidity of the deposit.

In a lead fluosilicate electrolyte we have no monovalent lead ions corresponding to the cuprous ions of the copper sulphate solution.

I electrolyzed lead fluosilicate solutions with lead electrodes, with porous partitions to separate the anode and cathode compartments, so that I had a concentration cell, after some hours electrolysis, of which I could measure the e.m.f. The work was not done accurately, as I had no facilities for very delicate work, but I found in general that with gelatine present in the solution the e.m.f. of the concentration cells was from one-third to one-half as great as when no gelatine was present.

The same experiment repeated with the silver nitrate solution and silver cyanide solution, run in the same circuit, would be interesting. I should suggest that before reading the e.m.f. the current should be reversed for a very short time, so that electro-deposited metal will be present on both anode and cathode, so that the difference of e.m.f. of solution between cast metal and electro-deposited metal need not be considered.

In the dissolution of an anode we have the exact reverse of the conditions at the cathode. A solution which will give projections at the cathode, ought for the same reason to give pits in the anode. In the dissolution of a lead anode in a fluosilicate solution I have noticed that with gelatine present the surface of the lead underneath the anode slime remains much smoother than in the absence of gelatine. This fact would seem to prove that the cause of projections at a cathode is not to be sought in the chemical composition of the deposit, but in the physics of the solution.

With regard to the question raised by Professor Bancroft, whether a high or low current-density favors a fine-grained deposit, it would seem that if, with increasing current-density, the e.m.f. of the concentration cells increased more rapidly in proportion, then a low current-density would give a better deposit, while if this e.m.f. increases in less proportion a high current-density would be more favorable.

I hope that we can have some more experiments along these lines.

Prof. Louis Kahlenberg: Where so many factors enter into a question as in this case, it is difficult to arrive at general conclusions; this is evident from the paper and also from the discussion so far as it has gone. I think it will be recognized that we have here touched upon one of the important questions of electrochemistry. It is evident that a vital point

in determining the physical character of an electrolytic deposit is the composition of the solution—the chemical make-up, if I may use the term, of the solution. Current-density, difference of potential, and temperature, all enter in as important factors to be sure; but if the chemical composition is not right, regulation of temperature, current-density, and e.m.f. will not give us the desired deposit. Attempts to get a dense smooth deposit of silver from an aqueous solution of silver nitrate do not succeed; the deposit is always crystalline no matter at what temperatures or current-densities the electrolysis proceeds. Neither does varying the strength of the solution or the e.m.f. result in producing a non-crystalline deposit. On the other hand, a silver nitrate solution in pyridine will always yield a dense, non-crystalline deposit. That increase in solubility improves the character of the deposit, as has been claimed, seems plausible from a number of cases. But it would be difficult to obtain a salt more soluble than silver nitrate in water, and yet, a smooth, non-crystalline deposit does not form when the aqueous solution of this salt is subjected to electrolysis. Furthermore, I am not pursuaded that it will be possible to maintain the general statement that high current-density and high potential difference always tend to yield a better deposit. Indeed it is well known that just the opposite has frequently been claimed as true. I believe the study of this question is not based upon a sufficient number of cases. We should not be too ready to draw general conclusions from a few isolated experiments.

It seems to me that Professor Bancroft has made a good beginning, but, as he himself admits, definite conclusions have not yet been obtained. Further work in this direction should be encouraged, and every one interested in electroplating ought to give it his careful consideration.

I am not at all sure what Professor Bancroft means by the term "soluble" as he uses it. Does he mean the amount of substance taken up by a given quantity of solvent, or the rate at which a substance dissolves? If the latter, this would depend, of course, upon temperature, surface exposed, stirring, as well as upon the nature of the substances concerned. It seems to me that this point should be carefully defined.

I may say, in regard to the matter of the adhesion of the electrolytic deposit as influenced by the affinity existing between the plating and the underlying metal, that the experiments of Roberts-Austen on lead and gold show conclusively that metals do penetrate into each other, in other words, that they do have affinity for each other, and that this is a factor which we can not ignore; although, as has been explained, changes of conditions, particularly those of temperature, may cause crystallization to set in resulting in disruption of the joint or union which under other conditions would remain quite secure.

Mr. Edw. F. Kern: If I am permitted, I would like to make a reference to a paragraph in a paper read by Mr. Anson G. Betts at the Albany meeting of the Mining Engineers in February, 1903, in regard to the smoothness of the cathode: "The smoothness and the purity of the deposited lead are proportional. Most of the impurity seems to be introduced mechanically through the attachment of floating particles of slime to irregularities on the cathodes. The effect of roughness is cumulative;

it is often observed that particles of slime attract an undue amount of current, resulting in the lumps seen on the cathodes. Samples taken at the same time showed from 1 to 2.5 oz. silver per ton in very rough cathodes, 0.25 oz. per ton as an average for smoother cathodes, and only 0.04 oz. in samples of cathodes selected for their smoothness."

I would also like to refer to the paper on "The Lead Voltameter," by Mr. Betts and Mr. Kern, in regard to the current-density and strength of solutions. This will be presented later, but it might be well to present this part now. By looking over the table you will see that the current-density used was from 7 to 37 amperes per square foot, and that the results are as accurate where large current-densities were used as with the smaller. We have here in one case employed a current-density of 37 amperes per square foot and in another 7.5 amperes per square foot. The smoothness of the deposit in both cases is about the same, irregardless whether a strong or weak electrolyte was used.

Now, in regard to the paper that has been read: Several years ago, while a student at the University of Pennsylvania, I carried out a research attempting to separate nickel and cobalt. This was done by converting the cobalt into potassium cobalti-cyanide similar to the formation of potassium ferri-cyanide in solution. The experiment I made did not come out as I expected, but I found that by the addition of potassium cyanide to an alkaline electrolyte of nickel, the deposit of nickel formed was smoother than that obtained by using other solutions. The addition of ammonium carbonate in place of ammonia produced smoother deposits when from 1 to 2 per cent of cyanide was present.

Prof. Louis Kahlenberg: When nitrate of lead is dissolved in pyridine, you always get a smooth deposit of lead, although the salt is but sparingly soluble in that solvent.

Mr. Edw. F. Kern here exhibited a sample of lead, and said:

We have obtained lead an inch thick just as smooth as that. I only brought that because it is light.

Prof. C. F. Burgess (in the chair): We ought to be thankful for a paper of this sort for our consideration. The electroplating industry is perhaps the oldest industrial application of our electrochemistry, but electrochemistry, at the present time, is in a most unsatisfactory condition as regards its literature. It has already been pointed out that when attempts are made to repeat experiments of others, in accordance with published directions, the result is frequently a failure. Especially is this true when good metal deposits are sought; but the failure to repeat the performances of others is due usually to incomplete description of all the conditions rather than to misrepresentation.

There are many varying factors that must be taken into account, and it is exceedingly difficult to classify them and tell what the variation of a single factor will produce in results. Doctor Bancroft has summarized in Table I the various materials which are employed in the production of good metal deposits, and he has thrown some light upon the reasons for using some of them. In regard to Doctor Bancroft's conclusions, I have no doubt that most of us who have studied the deposition of metals can recall instances which contradict his conclusions and cause us to differ

with him. But that is not necessarily criticism upon his paper, because most of the results will come under his scheme.

I would differ with the author in his statement on the first page that "neither the analyst nor the refiner cares about the smoothness of the deposit, so long as no trees are formed." As far as the refining is concerned, it is a preeminent requisite that the deposit shall be smooth. It must be smooth after the deposition has proceeded 24 hours, and after running 48 hours or even longer. Most electrolytic deposition for refining purposes requires 20 days, or more, which means that during the first few days, or even weeks, the depositions must be smooth, or otherwise you could never carry the depositions long enough to give a thick deposit. This difference of opinion is simply due to the difference in definition of what a bad deposit is. I would say, looking at it from the standpoint of the electrorefiner, that any deposit not laid down in a smooth layer is a bad one. Of course, from the electroplater's standpoint, a solution might give good deposition, while from the refiner's standpoint, it would give a bad deposition. Before attempting to classify the factors producing bad deposits it is necessary to define more clearly what bad deposits are.

Mr. Edw. F. Kern: Referring to the sentence that "Neither the analyst nor the refiner cares about the smoothness of the deposit, so long as no trees are formed." The electrolytic lead refiner does care, for the smoothness of the deposit indicates the purity of the product. The smoother the deposit, the purer the product. In refining lead by the Betts process, you ought to get lead which will equal a purity of about 99.999 per cent. This you are able to get right along so long as you work to get smooth deposits, and we always work to that end and succeed in getting lead of the highest purity.

Prof. C. F. Burgess (in the chair): In Mr. Betts' discussion is pointed out the rather surprising fact that impurities collecting on the cathode serve to attract the current. This is surprising, since these impurities are usually non-conductors and would be expected to resist rather than facilitate the flow of current to those localities where they adhere. There is no doubt that such impurities become covered by a mound of metal, but it does not seem to me to be due to the attraction of the current, but rather to the high current-densities around the insulating material, and consequent coarse crystalline deposit which finally bridges over.

Mr. Edw. F. Kern: I would just like to mention that it seems to me that the particles of slime do not actually attract the current, but that they tend to conduct it. You get certain impurities, especially in lead refining, such as silver, antimony, bismuth and copper; these are in the slime as metals and conduct the current better than the lead, and probably this is one reason why the rougher deposits are less pure. The lumps indicating where particles of slime have attached themselves. Of course in copper refining you have sulphur in the slime, which acts as an insulator.

Dr. W. D. Bancroft: Mr. Betts says that the experiments of Glaser are not accurate and that he has not been able to duplicate them. Glaser's account of his own work reads like a straightforward statement of experimental results. In the absence of any evidence to the contrary I assumed

that he was describing what he found. If he was not, of course that part drops out, and I shall take pains to verify that. I do not really see the advantage in the quotation of some of the experiments giving the conditions under which Glaser did not get a good deposit, because these are not the subject of dispute at all. Then Mr. Betts states that Glaser does not make the generalization that a reducing agent improves the equality of the deposition. When I get back to Ithaca, I shall be happy to give the page reference.[1] In the case of cadmium and zinc, the deposition of small quantities of cadmium with the zinc is said to make the zinc deposit bad. Of course this statement postulates that the cadmium precipitates as metal. I am inclined to believe either that the cadmium precipitated as hydroxide or that the zinc and cadmium formed a local couple oxidizing the zinc. Instead of testing for hydroxide, Mr. Betts has preferred to ascribe a mysterious power to metallic cadmium. Mr. Betts objects to my statement that the addition of gelatine or glue improves the quality of the deposits, and says that his own experiments with lead show that he could not get a good deposit in that way. A little later on, in objecting to my statement as to reducing agents, he takes the opposite view. Mr. Betts apparently believes that glue has a good effect when added as a reducing agent and a bad one when added as a colloid.

Mr. Betts says that, in the absence of any experimental evidence, he thinks a low current-density gives small crystals. That would be all right if it were in the absence of experimental evidence. As far back as 1837, experiments were made by Golding-Bird in which a coarsely crystalline structure was obtained when a very low current-density was used. Similar experiments were made at a more recent date. As I stated in my paper, I have myself had a number of experiments made to test this particular matter, and we have some photo-micrographs showing the results. To draw accurate conclusions in regard to crystals, a microscopic examination should always be made.

The question of solubility, raised by Mr. Kahlenberg, seems to be based on a misunderstanding. I thought I was clear in what I said. I did not refer to the solubility of the metallic salt in the solvent. I spoke of adding something which would dissolve the oxide or hydroxide. This has nothing to do with the solubility of silver nitrate, for instance, in pyridine or water. As regards the rate of solution, the disturbing salt must dissolve faster than it precipitates, if one is to get good results. The experiment cited by Mr. Kern of cyanide solution is covered by my paper. If we add potassium cyanide we increase the potential difference between the metal and the solution. Consequently, we get much finer deposits. It is generally known that most metals precipitate well from cyanide solutions. I refer to this specifically in my paper. As regards the other point that seems to be at issue, whether the refiner requires a smooth deposit in the sense that the plater does, I call your attention to the sample of lead which has been passed around. It is smooth from the point of view of the refiner, but I doubt whether any of you will call it smooth from the standpoint of the electroplater. You can take any copper cathode

[1] *Zeit. Elektrochemie*, 7, 386 (1900).

plate, and one which is smooth from the point of view of the refiner is a series of mountains from the point of view of the plater. Mr. Burgess says that every one of you can recall cases which contradict the rather crude outline which I have given. I shall be very much obliged, indeed, if those of you who do recall these cases will give me a memorandum of them at some time—either here or send it to Ithaca—for I should like very much to go over them to see whether they are really contradictions, or whether they are based merely upon a misunderstanding of the facts. There are a good many points in my article on which I do not care to lay much stress; but on the other hand, as you know, there have been no end of experiments in plating, and we are not very much further ahead than before. Now, if we can get anything which will give us a definite thing to test for, and can get further experiments in plating carried out in a rational way, and either prove or disprove something, it will not be long before we shall actually come out with a theory of plating which will be accurate, even in details.

The following paper was then read by Prof. C. F. Burgess, in the absence of the authors:

Prof. W. D. Bancroft in the chair.

THE CARBON CELL.

BY PROF. DR. F. HABER AND DR. L. BRUNER, *Technical High School, Carlsruhe, Baden.*

Among the various attempts to construct galvanic cells in which an electric current is produced by the consumption of carbon, there is none that has been of greater interest than the experiment of Jacques, who proposed the cell consisting of the following:

Carbon — fused sodium hydrate — iron.

This cell has been the subject of experiments by numerous investigators, especially Mr. C. J. Reed in America, and Messrs. Liebenow and Strasser in Germany. Experiments which we ourselves have conducted show that the true nature of this cell is different from what it was supposed to be.

Let us consider first the behavior of each of the electrodes separately.

The iron electrode in the fused sodium hydrate is gradually covered with a protecting layer or skin of the oxide. As soon as this has been produced, the iron is no longer attacked, whereas previously it went into solution in the fused salt as iron oxide, with the development of hydrogen gas. This protecting skin can be produced rapidly if the iron is dipped for a short time into fused saltpetre, and subsequently carefully freed from the saltpetre by means of water.

The iron thus coated with this protecting skin, is called "passive" because the fused sodium hydrate produces no further changes on it.

This passive iron represents an oxygen electrode on which the atmospheric oxygen acts similarly, but better, than on a platinized platinum electrode dipped into an aqueous conducting solution. This action of the oxygen is brought about by the presence of sodium manganate, which is always present in small quantities in fused commercial sodium hydrate, and especially when in contact with iron, and its presence can easily be proved chemically. Quite pure sodium hydrate, when fused and in contact with commercial

iron, will contain some manganese because a small quantity of manganese forms a normal part of commercial iron and gets into the fused salt when the iron is attacked by the sodium hydrate previously to the production of the passive state; by means of the atmospheric air it becomes a manganate.

The passive iron, as an unattackable electrode, can be replaced by another indifferent electrode, as for instance by platinum, without changing the force and the method of action of the electrode in fused sodium hydrate containing manganese.

If platinum is placed into pure sodium hydrate the potential at the electrode is uncertain. A very small quantity of a manganate suffices to give rise to a different value, which does not change during a further addition of a manganate up to 2 per cent of the weight of the sodium hydrate.

If the added sodium manganate is reduced by forcing in some hydrogen or carbon monoxide, or by the addition of sodium oxalate or sodium formate, quite an extraordinary change will take place in the potential. But by forcing in some atmospheric oxygen the original value of the potential is again reached.

In these experiments the potential of the platinum electrode is thus brought about by the absorption of oxygen. If a permanagate is added to fused sodium hydrate, oxygen will be evolved and the potential will, contrary to the other case, be brought about by the evolution of oxygen. These potentials are measured most simply by letting the syphon of a decinormal-electrode terminate in a small vessel containing concentrated sodium hydrate, which is in electric contact with the fused salt which is to be tested, by means of a rod of solid sodium hydrate. In all the measurements the fused salt was in a large silver crucible. The observed values for different temperatures are collected in the following table. The temperature was measured thermoelectrically.

Centigrade degrees.....	312	336	360	388	412	472	532
Potential in volts against decinormal-electrode .	—0.265	—9.294	—0.314	—0.333	—0.353	—0.431	—0.472

These values were measured with a platinum electrode, a small quantity of the manganate being added to the sodium hydrate. Numerous tests showed that absolutely equal values of the potential are obtained with an electrode of passive iron. An earlier opinion from other sources, that the presence of certain steps in the oxida-

tion of the iron in the fused salt is of importance in the behavior of this electrode, is proved to be not correct.

Let us now consider the carbon electrode.

When a carbon electrode is tested in the way above described for iron and platinum, all possible values can be observed between — 0.6 and — 1.5 volts toward the decinormal-electrode. With closer study one finds that the potential approaches the value — 1.5 volts more and more, the more rapidly the carbon is attacked by the fused sodium hydrate with the evolution of gas. This attack is less the denser and the more graphitic the carbon is. Electrodes which are treated by the process of the International Acheson Graphite Company, therefore, remain very far from this value — 1.5 volts. Ordinary arc light carbons on the other hand can generally be made to produce a free gas evolution when the fused salt in which it is dipped is heated to above 500 deg. C. They then reach quite or nearly the value — 1.5 volts and remain at this value when the fused salt in which they are dipped is cooled to the point of solidification. But as the accompanying evolution of gas gradually diminished at a lower temperature (about 350 deg.), the potential will simultaneously change; it will diminish to the values — 1.3 or — 1.2 volts, etc.

The gas which the carbon electrode evolves in the hot fused sodium hydrate is hydrogen gas.

If, instead of the carbon electrode, a platinum tube is dipped into the fused sodium hydrate, and pure hydrogen gas is led through it into the liquid, one obtains with a strong current of gas the potential — 1.5 volts, and this will be the case at all temperatures between 500 deg. and the point of solidification of the fused salt. If the current of hydrogen gas is made weaker, the value — 1.5 volts will not be reached; the figures will be smaller. The potential of the carbon in the fused sodium hydrate is, according to this, not determined directly by the carbon, but by the hydrogen which the action of the carbon on the fused salt sets free. The temperature produces no effect on the potential within the given wide range, but the rapidity of the evolution of the hydrogen is of great importance.

Before we recognized this connection between the two, we had held a different conception concerning the process at the carbon electrode. We supposed that a formic acid salt or an oxalic acid salt, or carbon monoxide were produced, and that these materials

determined the potential at the carbon electrode. We, therefore, tested the action which an addition of the two named salts or the introduction of carbon monoxide had on the fused salt, and on the behavior of the platinum electrode which is dipped into the fused salt. We found by chemical investigations that former statements in the literature were confirmed, according to which oxalates and formates in an excess of fused sodium hydrate, pass over freely into carbonate and hydrogen gas. Formates may be assumed to be a combination of carbon monoxide with sodium hydrate, and oxalates may be assumed to be a combination of carbon monoxide with an alkali carbonate. We assumed, therefore, that carbon monoxide with sodium hydrate could also produce hydrogen and sodium carbonate. We found this to be definitely proved to be a fact, when we led carbon monoxide through a silver spiral heated to 350 deg., in which there was fused sodium hydrate. The following reaction is thereby obtained with great ease:

$$-CO + 2NaOH = CO_3Na_2 + H_2.$$

It can be proved by means of thermodynamics, that the oxalate, the formate and carbon monoxide, when they act as such on the electrode, should manifest their potentials, which exceed -1.5 volts. Such potentials, however, were never observed. On the other hand it was found that all three materials as such were inactive at the electrode, and that it was only the hydrogen evolved by them which charged them and brought their potential more or less closer to the value -1.5 volts, according to the rapidity of the release of the gas. According to these principles we are in a position to say that the so-called Jacques carbon cell is a hydrogen-oxygen chain, in which the oxygen of the air, by the intermediate action of the manganates at the iron electrode, acts with the hydrogen released by the carbon from the fused salt at the other electrode. The power of this element depends on the consistency of the carbon. If the latter is loose and capable of producing hydrogen gas evolution, one obtains those values which are found when one deducts -1.5 volts from the above-mentioned values for the oxygen electrode. As for instance $(-0.265 + 1.5)$ that is $+1.24$ volts at 312 deg. C, and $(-0.472 + 1.5)$ that is $+1.03$ volts at 532 deg. C.

Thermoelectric phenomena take no part in the production of these electromotive actions. For these forces do not depend in the least on the materials iron and carbon, but only on the gases

oxygen and hydrogen, and the same platinum tube shows alternately the force of the iron and the carbon electrode, if at constant temperature we pass through it oxygen and hydrogen respectively.

The element under discussion is without importance from the practical standpoint, because during its action the valuable carbon electrode and the equally expensive sodium hydrate are changed into cheap soda, only to obtain a little hydrogen which acts electromotively.

From the theoretical standpoint such a hydrogen-oxygen chain offers very much of importance. It is differentiated from the old well-known Grove hydrogen-oxygen chain, in that it is not liquid water, but a solution of water in fused sodium hydrate, which is produced by its action.

The relation which Helmoltz has proved for the connection between the electromotive force of reversible galvanic chains, and the reaction heat of the process which produces the current, enables us to calculate the heat of reaction in the present case. This is shown to be 81,650 gram calories per gram molecule of water produced. But as the formation of a gram molecule of water vapor at the range of temperatures of the experiment sets free approximately 58,650 gram calories, it follows that the evolution of heat which accompanies the absorption of a gram molecule of water vapor by a very large quantity of fused sodium hydrate has a value of approximately 23,000 gram calories. This high value arises from the fact that fused sodium hydrate holds the last traces of water with unusual tenacity, as has already been shown by others.

One can carry out the theoretical conception on the basis of the Helmholtz relation above given, in still another way. One can, for instance, suppose at the start that an equilibrium exists between a fused salt containing water, and the vapor pressure of the water above it. In this way one arrives at the conception that the action of our chain depends on the change of the atmospheric oxygen, which has a pressure of 0.2 atmosphere, and the hydrogen which has an atmospheric pressure, into water vapor of a pressure corresponding to the state of equilibrium above the water containing the fused salt. When we integrate the above-mentioned differential equation of Helmholtz, and for comparison consider the known values of the force of the Grove gas chain, we can calculate the vapor pressure above the fused sodium hydrate at different temperatures. The carrying out of these theoretical calculations re-

quires a more extended representation of the case and this departs too far from the intention of this discussion, to be embodied here. One can find it in an extended treatment of the subject which has appeared in the German language in the *Zeitschrift für Elektrochemie.*[1] The result of the calculations is that the vapor pressure above fused sodium hydrate at 300 deg. is extremely small and increases with increasing temperature. The fused mass is, therefore, especially hygroscopic near its point of solidification, and the force of the hydrogen-oxygen chain at this temperature is the highest. That the force of the Jacques carbon cell increases with the temperature is not in contradiction with this, but is explained according to our former statement by the fact that the evolution of hydrogen by the carbon increases in rapidity very quickly with increasing temperature.

Discussion.

The following communication by Mr. C. J. Reed, on the subject of the paper of Messrs. Haber and Bruner, was presented by Professor Burgess in Mr. Reed's absence:

I would call attention to the fact that the so-called Jacques cell was invented, not by Jacques, but by Henri Adolphe Archereau of Paris, who obtained for it British patent No. 1037, Feb. 26, 1883.

According to this paper the cathode of the cell consists of a film of iron oxide, which is not reduced by the electrolytic action but merely acts as an absorber of oxygen remaining itself unreduced. It would have added greatly to the interest of this paper if the authors had given some of the proofs of this statement, or at least indicated the nature of the experimental evidence on which the statement is based. Prof. Elihu Thomson[1] states as a result of his experiments that the action of the cell is to reduce this film of iron oxide to metal and the action of the injected oxygen is to reoxidize the reduced iron. All of my experiments have confirmed this. The film of oxide is always rapidly reduced on the passage of current to a film of metallic iron which has a characteristic grayish blue color and a powerful reducing action.

The statement in the paper that there is a permanent layer of iron oxide which acts as a cathode by absorbing and giving up oxygen, without itself undergoing electrochemical change, seems to me a most remarkable one and one that requires at least some proof. The authors do not even indicate the nature of the experimental evidence on this point if they have found any.

The paper states that this alleged peculiar behavior is brought about by the presence of sodium manganate, but does not state nor give us even a hint as to the manner in which the manganate accomplished this impor-

1. 1904. Vol. X, page 69F.

[1]*Jour.* Franklin Institute, Nov., 1896.

tant function, whether it is by chemical or electrochemical action or merely by its *presence.*

If the action of the manganate is merely by its "presence" and is not chemical or electrochemical, then the minute quantity of manganese said to be present, or even a single molecule, would be as amply sufficient as a larger quantity. But if the manganate has any chemical or electrochemical action, it is absurd to talk of manganate, in quantities so minute that, at most, only some thousandths of a milligram could be in contact with the cathode, transmitting currents of hundreds of amperes such as have been taken continuously for hours from these cells.

If (for the sake of argument only) we admit the allegations of the paper in regard to manganese and iron-oxide films, there is still no explanation on any theory except that of thermo-electric action, of the fact that an iron rod may be substituted for the carbon rod with the production of an even greater e.m.f., amounting to as much as 1.15 volts.[2] Nor is there any explanation of the fact that a current of illuminating gas produces substantially the same effect as a current of air;[3] nor of the production of the current by the use of a crucible of pure silver instead of the iron pot and of sodium hydroxide made from metallic sodium free from manganese and all other impurities.[4]

The probable electrochemical reaction in the cell has been very clearly stated by Ostwald.[5]

He describes the reaction in the zinc-copper-oxide cell as the strict analogue of the Jacques cell, and the paper before us does not seem to me to contain anything which controverts the position taken by Ostwald. In order that there may be no misapprehension, and because Ostwald's statement is exceedingly clear, exact and positive, I will quote his words:

"We possess in this cell the complete analogue of the Jacques cell. The rôle of the zinc is played by carbon, the rôle of the oxide of copper by ferric oxide, or by sodium ferrate. The cell will work until one of the three necessary constituents is exhausted. Since, according to Jacques, ferric oxide is the constituent present in the smallest quantity, the activity of the cell depends entirely upon the renewal of the exhausted ferric oxide, i. e., on the amount of air or oxygen which is conveyed to the iron cathode.

"If we were to construct the Lalande cell with plates of porous metallic copper instead of copper oxide, we should then be able to obtain from it a current only in proportion as fresh copper oxide is generated, say by the blowing in of air to the cathode, or by allowing it to partially project in the air, and giving it a slow rotary movement, in such a manner that the reduced parts should be practically exposed to the air.

"As may be seen, in this cell as well as in the Jacques cell, the only active substance is the absorbed oxygen, and the energy which is set free by the union of the oxygen with the copper or the iron, is lost as far as the electrical process is concerned. There is practically no way known as

[2] *Electrical World,* July 25, 1896.

[3] *Trans.* Am. Inst. of Electrical Eng., Apr. 27, 1898.

[4] *Jour.* Franklin Inst., December, 1898.

[5] *Am. Electrician,* January, 1898.

yet for preventing this loss. If the cathode of the Jacques cell consisted of any nonoxidizable metal which would simply absorb the oxygen, as palladium absorbs hydrogen, a far higher e.m.f. might be secured, because in this case the potential of free oxygen of the air, which is very high, would become effective. Free oxygen, however, is unfortunately a substance which, despite its high potential, reacts very slowly, and in order to realize practical velocity of reaction, we must put up with the loss of potential resulting from the oxidation of copper or iron."

No theory could be more explicit as to the electrochemical reaction or harmonize better with observed facts than this statement of Ostwald.

The source of the e.m.f. is therefore a question of the energy of this electrochemical reaction. If the complete electrochemical reaction of the cell, including necessarily the chemical change at both electrodes, viz., the oxidation of the carbon and reduction of iron oxide, evolves energy, that energy will produce an e.m.f. in the direction of the current. If this complete electrochemical action absorbs energy, it will oppose an e.m.f. to the current and the e.m.f. producing the current must necessarily originate in some other source than the electrochemical action.

The only possible electrochemical reaction, according to Ostwald's statement quoted above, is the reduction of an oxide of iron by the oxidation of carbon. Whether the carbon be oxidized to CO or CO_2 and whether the iron be reduced to the metallic state from an oxide, or reduced from a higher to a lower oxide, the energy of the carbon alone in either case is not sufficient for the reduction of the iron and can not, therefore, supply any excess in the form of electrical energy. There is only one other source of energy present, viz., the heat used in maintaining the high temperature. How can we escape from the conclusion that the heat is the source of the e.m.f. We must keep in mind that the energy of an equivalent carbon is less than the energy of an equivalent of iron and that an equivalent of iron can not be reduced by the energy of an equivalent of carbon, there being always required the energy of additional carbon burned in an additional independent reaction.

The thermo-chemical equations of the various possible reactions in this cell have been given by me elsewhere,[6] and if manganese were substituted for iron the electrochemical action would require even greater absorption of energy.

Measurements of potentials alone can not determine the electrochemical reaction of a cell. The measurements of temperatures and potentials given in this paper, however, show very clearly that the e.m.f. is not only dependent upon, but is directly proportional to, the temperature, as would be expected if the action were thermo-electric. The statement that "the temperature produces no effect on the potential within the given wide range" is a denial of the figures given in the paper, as well as a denial of our generally accepted conclusions thermodynamically deduced.

If I understand the authors correctly, the claim is that the e.m.f. of the cell originates in the union of free oxygen and free hydrogen and that the intensity of the e.m.f. is proportional to the rapidity with which the

[6] *Electrical World*, Jan. 2, 1897.

hydrogen is evolved and that this increases with the temperature. This is certainly a new theory of e.m.f.—that it is proportional to the quantity of the chemical reagent present.

I would ask where the hydrogen for this supposed reaction comes from? The paper says it is reduced by the carbon, but this can not occur without the absorption of heat, as will be seen by an inspection of the following thermochemical reaction:

$$\overline{C + H_2O} = \overline{CO + H_2}^{\,69 \qquad 29}$$

$$\overline{C + 2H_2O} = \overline{CO_2 + 2H_2}^{\,2 \times 69 \qquad 97}$$

The first reaction absorbs heat corresponding to $\frac{69 - 29}{2 \times 23.24} = 0.86$ volt, and the second to $\frac{2 \times 69 - 97}{4 \times 23.24} = 0.44$ volt. Where does this energy come from if not from the applied heat?

It seems to me there is a broad method of determining the source of e.m.f. in this cell, without reference to potential differences. If the energy of the current is derived from heat, the process must be thermo-electric. If it is derived directly from chemical energy, it is electrochemical or galvanic. The only possible source of chemical energy in the cell is admitted to be the oxidation of the carbon. If the carbon is directly oxidized by free oxygen, the process is combustion and produces only heat. In order to be electrochemical, the oxidation must be accomplished by oxygen derived from a preexisting oxide and by the decomposition of the electrolyte at both terminals, as in all other electrochemical reactions. Even in the Grove gas cell the oxygen and hydrogen must first combine with platinum before they can produce electrochemical reaction. With carbon electrodes, instead of platinum, the oxygen-hydrogen cell gives no e.m.f. and no electrochemical reaction. In the so called Jacques cell there is no oxide present which carbon can decompose without absorbing energy. The energy of combustion of the oxygen and reduced iron at the cathode, as Ostwald says in the passage quoted above, "is lost as far as the electrical process is concerned." As there is no possible electrochemical action present in the cell except those which absorb energy, the energy of the cell must be derived from heat.

Dr. W. D. Bancroft (Chairman): Experiments made in my laboratory several years ago showed that the carbon dissolved quantitatively, which does not seem quite compatible with very small reactions between oxygen and hydrogen; and further, I should think it might be interesting to learn what would happen in case the caustic soda were replaced more or less completely by sodium carbonate. Of course the temperature would be very much higher. Personally, I think the caustic soda is necessary for the reaction.

Doctor Kahlenberg: Do you say the carbon dissolves quantitatively or simply disintegrates?

Chairman: It dissolves very nearly quantitatively.

The following paper was then read by the author:

THE ELECTROCHEMICAL SERIES OF THE METALS.

BY PROF. LOUIS KAHLENBERG, *University of Wisconsin. Delegate of the American Electrochemical Society.*

The current conception of the electrochemical series of the metals is the arrangement of the latter in a series so that any metal will be electropositive to all that follow it, and electronegative to all that precede it; and that any member of the series will chemically replace all the metals that follow it, and in turn be replaced by those that precede it in the series. In seeking combinations of metals that would produce the highest electromotive forces, Volta discovered the possibility of arranging metals in an electrochemical series; though, as pointed out by Ostwald in his history of electrochemistry, he did not at first realize that he had thus discovered a fundamental property of the metals.

Since the time of Volta the electrochemical series of the metals has figured with more or less prominence in all treatises on chemistry and electrochemistry. The position of the metals in the series is determined by their replacing power, but particularly by the difference of potential existing between the metals in contact with each other, or better in contact with an electrolyte. The electrolyte usually employed is a solution of some salt or acid in water. It has long been known that the character of the acid or salt and the strength of the solution used exert an influence upon the difference of potential between the metal and the solution. This point is well discussed by Jahn in the opening pages of his treatise on electrochemistry. Nevertheless, the general feeling with regard to the electrochemical series at present is that it really represents a fundamental property of the metals, and that, though the character of the electrolyte into which the metals are dipped when the electromotive forces are measured, affects the electrochemical series somewhat, such effects are but slight, and the order of the metals in the series remains essentially the same in all cases.

This view has no doubt been strengthened by the theory of Nernst, according to which each metal is endowed with an electrolytic solution tension, an inherent property of the metal tending to drive it into the solution into which the metal dips, and which varies only with the nature of the solvent employed in forming the solution. The theory of Nernst postulates the theory of electrolytic dissociation, and it is conceived that that which operates against the hypothetical solution tension of the metal is the so-called osmotic pressure of the simple ions of that particular metal in the solution. On the basis of this view, it would naturally be expected that the difference of potential between a metal and a solution of its salt would always be the same, no matter what other things might be contained in the solution or what solvent might be used, as long as the concentration of the ions of the particular metal in question remained constant. A few preliminary experiments made by Jones,[1] however, soon showed that it was necessary to assume that the electrolytic solution tension of a metal varies with the nature of the solvent.

During the last six years the differences of potential between metals and solutions, particularly such solutions in which water is not used as a solvent, have been one of the subjects of study in my laboratory.[2] In the course of these investigations, there were employed, besides carbon, twenty different metals as electrodes; thirty-five different solvents were used in making up the solutions; and fifteen different salts were employed as solutes. The metals serving as electrodes included all of those in common use, while the solvents and solutes selected represented, as far as possible, typical substances. In the selection of the solvents and solutes, the questions of securing sufficient solubility and electrolytic conductivity necessarily influenced the choice very greatly.

The outcome of all this work is the establishment of the fact that at a fixed temperature the difference of potential between a metal and an electrolyte depends upon the character of the metal and upon the composition of the electrolyte. Not only does the character of the solvent affect this difference of potential, or, if the theory of Nernst and the theory of electrolytic dissociation be assumed, not only does the osmotic pressure of the simple ions of

1. *Zeit. Physik. Chem.* 14, 346 (1894).
2. Compare *Jour. Phys. Chem.* 3, 379 (1899); Ibid., 4, 709 (1900); also *Trans.* Amer. Electrochem. Soc. 2, 89 (1902).

the metal in the solution and the so-called electrolytic solution tension of the metal determine the difference of potential, but *every* ingredient used in making up the solution affects this difference of potential to some extent, and frequently very materially indeed. Nor would the assumption of so-called complex ions, or of an influence which the solutes might have on the concentration of the ions of the metal in question (for which assumptions there would moreover frequently be no grounds) enable one to escape from the conclusion that the electrolytic solution tension of a metal is influenced not only by the solvent but also by the solute. But if the electrolytic solution tension of a metal is determined by the character of the solvent and also by that of the solute, it is plainly evident that this quantity, which is viewed by Nernst as an inherent property of the metal itself, is in reality as much a function of all the ingredients in the electrolyte as of the metal. In this connection it is of fundamental importance to bear in mind a further result of the investigations carried on here, namely, that the change which the difference of potential between a metal and the surrounding solution undergoes when any constituent of the solution is altered, is in general different, either as to magnitude or direction, or both, for different metals toward the same solution.

The facts established experimentally in these researches point to the conclusion that the difference of potential between a metal and an electrolyte into which the metal dips is due to the mutual chemical interaction of electrode and electrolyte. On the basis of this view the facts at hand can readily be explained. It becomes clear at once why a change in any ingredients of the electrolyte should affect the e.m.f. developed, and why in the case of different metals this effect should be different as to magnitude or sign, or both, for one and the same change in the electrolyte. At first thought it might seem that this view of ascribing the e.m.f. developed at the junction between a metal and an electrolyte to the chemical affinity, or strain tending toward interaction, existing between the metal and the electrolyte, would not enable one to detect regularities existing in the phenomena of the electromotive forces that have actually been measured, but this is a delusion. Similar metals behave similarly in the development of potential differences toward an electrolyte, and similar ingredients introduced into an electrolyte produce similar effects toward one and the same metal in the development of potential differences. Bearing this in mind

enables one to detect much of regularity in the electromotive forces measured.

As a striking instance of how the difference of potential between a metal and an electrolyte changes when one of the ingredients of the electrolyte is gradually altered, the following illustration may be given. The e.m.f. of the chain: Ag $\left|\frac{N}{10}AgNO_3\right.$ in Pyridine $\left|\frac{N}{10}AgNO_3\right.$ in Water|Ag, is 0.422 volts at 20° C., the silver in the aqueous solution being the positive pole of the combination. When in the first half of the chain pyridine is gradually replaced by water, keeping the solution one-tenth normal for $AgNO_3$ and allowing everything else in the chain to remain unchanged, the e.m.f. of the combination varies as indicated in Table 1. The first column shows the composition of the electrolyte of the first half of the chain by indicating the number of volumes of one-tenth normal $AgNO_3$ in water used to one volume of one-tenth normal $AgNO_3$ in pyridine; and the second column gives the e. m. f. found. The silver dipping in the one-tenth normal $AgNO_3$ solution in water remains the positive pole throughout.

TABLE 1.[3]

Volumes of water.	E.M.F. in volts.
0.00	0.422
0.33	0.376
1.	0.339
3.	0.300
7.	0.259
15.	0.210
32.	0.148
64.	0.055
127.	0.022
255.	0.013
511.	0.011

During the past year I have had Mr. J. P. Magnusson, fellow in chemistry at this university, measure the differences of potential between various metals dipping in a one-tenth normal solution of

3. This Table is taken from one of the papers cited above, *Jour. Phys. Chem.* 3, 279 (1899).

lithium chloride. The solvents used in making up these one-tenth normal lithium chloride solutions were pure pyridine, pure water, and mixtures of pyridine and water in various proportions. Great care was used to have all the materials employed of a high degree of purity, and to have the surfaces of the metals free from contamination. In each case the chain measured was of the form, Metal | $\frac{N}{10}$ LiCl in pyridine, water, or pyridine + water | $\frac{N}{10}$ $AgNO_3$ in pyridine | Ag. The second half of the chain always remained unchanged; and for the value of this half of the combination I had previously found[4]—0.573 volt,[5] on the assumption that the half cell, —nKCl·HgCl | Hg is equal to —0.56 volt.

In Tables 2 to 6, which follow, the metal in the first half of the chain is indicated in the first column; in the second column is given the total e.m.f. of the chain indicated at the head of the table; and in the third column is given the difference of potential of the first half of the combination referred to the value —0.56 volt for the normal calomel electrode. In computing the values in the third column, careful attention was paid to the sign.

TABLE 2.

Chain: Metal | $\frac{N}{10}$ LiCl in pyridine | $\frac{N}{10}$ $AgNO_3$ in pyridine | Ag.

Metal.	Total E.M.F.	E.M.F. of first half.
1 Mg	1.211 volts	+0.638 volts
2 Zn	1.043	+0.470
3 Cd	0.966	+0.393
4 Mn	0.808	+0.235
5 Al	0.705	+0.132
6 Pb	0.663	+0.090
7 Sn	0.618	+0.044
8 Cu	0.595	+0.022
9 Co	0.548	—0.025
10 Ni	0.444	—0.129
11 Sb	0.438	—0.135
12 Bi	0.423	—0.148
13 Hg	0.411	—0.162

4. *Jour. Phys. Chem.* 3, 379 (1899).
5. This value was fully confirmed by Mr. Magnusson.

TABLE 2 — (*Continued*).

Metal.	Total E.M.F.	E.M.F. of first half.
14 Ag	0.398	—0.175
15 Cr	0.387	—0.187
16 Au	0.309	—0.264
17 Fe	0.288	—0.285
18 Pd	0.251	—0.322
19 Pt	0.199	—0.374
20 C	0.154	—0.727

TABLE 3.

Chain: Metal | $\frac{N}{10}$ LiCl in 1 vol. water + 3 vols. pyridine | $AgNO_3$ in pyridine | Ag.

Metal.	Total E.M.F.	E.M.F. of first half.
1 Mg	1.697 volts	+1.124 volts
2 Zn	1.244	+0.671
3 Mn	1.069	+0.496
4 Al	0.895	+0.321
5 Pb	0.650	+0.077
6 Cd	0.637	+0.064
7 Cu	0.568	—0.005
8 Co	0.542	—0.031
9 Sn	0.486	—0.087
10 Fe	0.402	—0.171
11 Sb	0.384	—0.189
12 Ni	0.365	—0.208
13 Bi	0.365	—0.208
14 Hg	0.194	—0.379
15 Ag	0.169	—0.404
16 Pt	0.156	—0.417
17 Cr	0.125	—0.448
18 Pd	0.119	—0.454
19 Au	0.101	—0.472
20 C	0.119	—0.692

TABLE 4.

Chain: Metal | $\frac{N}{10}$ LiCl in 1 vol. water + 1 vol. pyridine | $\frac{N}{10}$ $AgNO_3$ in pyridine | Ag.

Metal.	Total E.M.F.	E.M.F. of first half.
1 Mg	1.669 volts	+1.096 volts
2 Zn	1.247	+0.674
3 Mn	1.128	+0.555
4 Al	0.855	+0.281
5 Pb	0.698	+0.125
6 Cd	0.659	+0.086
7 Co	0.559	—0.014
8 Cu	0.528	—0.045
9 Sn	0.449	—0.124
10 Fe	0.411	—0.162
11 Sb	0.370	—0.203
12 Ni	0.336	—0.237
13 Bi	0.318	—0.255
14 Hg	0.106	—0.467
15 Cr	0.106	—0.467
16 Pt	0.074	—0.499
17 Ag	0.067	—0.506
18 An	0.006	—0.567
19 Pd	0.012	—0.585
20 C	0.121	—0.694

TABLE 5.

Chain: Metal | $\frac{N}{10}$ LiCl in 3 vols. water + 1 vol. pyridine | $\frac{N}{10}$ $AgNO_3$ in pyridine | Ag.

Metal.	Total E.M.F.	E.M.F. of first half.
1 Mg	1.662 volts	+1.089 volts
2 Mn	1.212	+0.639
3 Zn	1.188	+0.615
4 Al	0.828	+0.255
5 Cd	0.746	+0.173
6 Pb	0.669	+0.096
7 Co	0.548	+0.025
8 Cu	0.485	—0.088
9 Sn	0.436	—0.137

TABLE 5 — (*Continued*).

Metal.	Total E.M.F.	E.M.F. of first half.
10 Fe	0.417	—0.156
11 Sb	0.316	—0.257
12 Ni	0.316	—0.257
13 Bi	0.297	—0.276
14 Cr	0.082	—0.491
15 Ag	0.075	—0.498
16 Hg	0.056	—0.517
17 Pt	0.006	—0.567
18 Pd	0.006	—0.567
19 Au	0.015	—0.588
20 C	0.075	—0.648

TABLE 6.

Chain: Metal | $\frac{N}{10}$ LiCl in water | $\frac{N}{10}$ $AgNO_3$ in pyridine | Ag.

Metal.	Total E.M.F.	E.M.F. of first half.
1 Mg	1.666 volts	+1.093 volts
2 Mn	1.151	+0.579
3 Zn	1.111	+0.538
4 Cd	0.782	+0.209
5 Al	0.777	+0.204
6 Pb	0.697	+0.124
7 Fe	0.593	+0.020
8 Co	0.450	—0.123
9 Sn	0.403	—0.170
10 Bi	0.273	—0.300
11 Sb	0.271	—0.302
12 Cu	0.228	—0.345
13 Ni	0.189	—0.384
14 Ag	0.131	—0.442
15 Cr	0.065	—0.508
16 Pd	0.009	—0.564
17 Hg	0.020	—0.593
18 Pt	0.038	—0.611
19 Au	0.054	—0.627
20 C	0.067	—0.640

To facilitate comparison, the values in the third columns of Tables 2 to 6 are gathered together in Table 7, the headings of the columns of the latter table indicating the composition of the solvent used.

TABLE 7.

The electrolyte was $\frac{N}{10}$ Li Cl, the solvent used being indicated by the heading of each column.

Pyridine.	1 vol. water plus 3 vols. pyridine.	1 vol. water plus 1 vol. pyridine.	3 vols. water plus 1 vol. pyridine.	Water.
Mg +0.638	Mg +1.124	Mg +1.096	Mg +1.089	Mg +1.093
Zn +0.470	Zn +0.671	Zn +0.674	Mn +0.639	Mn +0.579
Cd +0.393	Mn +0.496	Mn +0.555	Zn +0.615	Zn +0.538
Mn +0.235	Al +0.321	Al +0.281	Al +0.255	Cd +0.209
Al +0.132	Pb +0.077	Pb +0.125	Cd +0.173	Al +0.204
Pb +0.090	Cd +0.064	Cd +0.086	Pb +0.096	Pb +0.124
Sn +0.044	Cu −0.005	Co −0.014	Co −0.025	Fe −0.020
Cu +0.022	Co −0.031	Cu −0.045	Cu −0.088	Co −0.123
Co −0.025	Sn −0.087	Su −0.124	Sn −0.137	Sn −0.170
Ni −0.129	Fe −0.171	Fe −0.162	Fe −0.156	Bi −0.300
Sb −0.135	Sb −0.189	Sb −0.203	Sb −0.257	Sb −0.302
Bi −0.148	Ni −0.208	Ni −0.237	Ni −0.257	Cu −0.345
Hg −0.662	Bi −0.208	Bi −0.255	Bi −0.276	Ni −0.384
Ag −0.175	Hg −0.379	Hg −0.467	Cr −0.491	Ag −0.442
Cr −0.187	Ag −0.404	Cr −0.467	Ag −0.498	Cr −0.508
Au −0.264	Pt −0.417	Pt −0.499	Hg −0.517	Pd −0.564
Fe −0.285	Cr −0.448	Ag −0.506	Pt −0.567	Hg −0.593
Pd −0.322	Pd −0.454	Au −0.567	Pd −0.567	Pt −0.611
Pt −0.374	Au −0.472	Pd −0.585	Au −0.588	Au −0.627
C −0.727	C −0.692	C −0.694	C −0.648	C −0.640

In order to compare these results with those of Neumann,[6] who measured the differences of potential between metals and aqueous solutions of their salts, the values he found are given in Table 8.

TABLE 8.[7]

	Volts.
Magnesium	+ 1.231
Aluminum	+ 1.015
Manganese	+ 0.824
Zinc	+ 0.503
Cadmium	+ 0.174
Iron	+ 0.087
Cobalt	— 0.015
Nickel	— 0.020
Lead	— 0.095

6. *Zeit. Physik. Chem.* 14, 229 (1894).

7. This table is taken from Neumann's paper, *Zeit. Physik. Chem.* 14, 229 (1894). The values recorded were obtained with the solutions of the chlorides of the metals except in the case of Cu, Hg and Ag where the sulphates were used. The solutions of the chlorides of Bi, Sb, and Sn contained excess of acid.

TABLE 8 — (*Continued*).

	Volts.
Bismuth	—0.315
Antimony	—0.376
Tin	—0.085
Copper	—0.515
Mercury	—0.980
Silver	—0.974
Palladium	—1.066
Platinum	—1.140
Gold	—1.356

Comparing the values in the first column of Table 7 with those in Table 8, it appears that the one-tenth normal lithium chloride solution in pyridine is less positive toward Mg, Zn, Mn, Al, Co, Ni, and Fe than are the aqueous solutions of salts of these metals, whereas for all the other metals the reverse is the case. In column 5, Table 7, the values for Mg, Mn, Al, Fe, Co, and Ni show that toward these metals the one-tenth normal lithium chloride solution in water is less positive than are the aqueous solutions of their salts (compare Table 8), whereas the reverse is true of the other metals. And again, when columns 2 to 4, Table 7, are compared with Table 8 the same will be observed for the metals just mentioned. Bearing in mind that the lithium chloride content of the solutions in Table 7 remains constant and that these lithium chloride solutions are more positive toward the metals just mentioned and less so toward the other metals, than are the solutions of the salts of the metals toward the latter (Table 8), it seems natural to conclude that the effect noted is due largely to the substitution of the lithium chloride for the salts of the metals.

A comparison of columns 1 and 5, Table 7, shows clearly the striking effect which a substitution of pyridine for water produces on the electrochemical series, and also on the absolute values of the potentials. The intermediate columns 2 to 4 show by what gradations the values of column 1 pass into those of column 5. These effects are different for different metals as is shown by the accompanying Figure 1, in which ordinates represent differences of potential and abscissas per cent of water by volume contained in the solvent used.

It is interesting to note in Table 7 that magnesium maintains itself at the head of the series throughout and carbon remains at

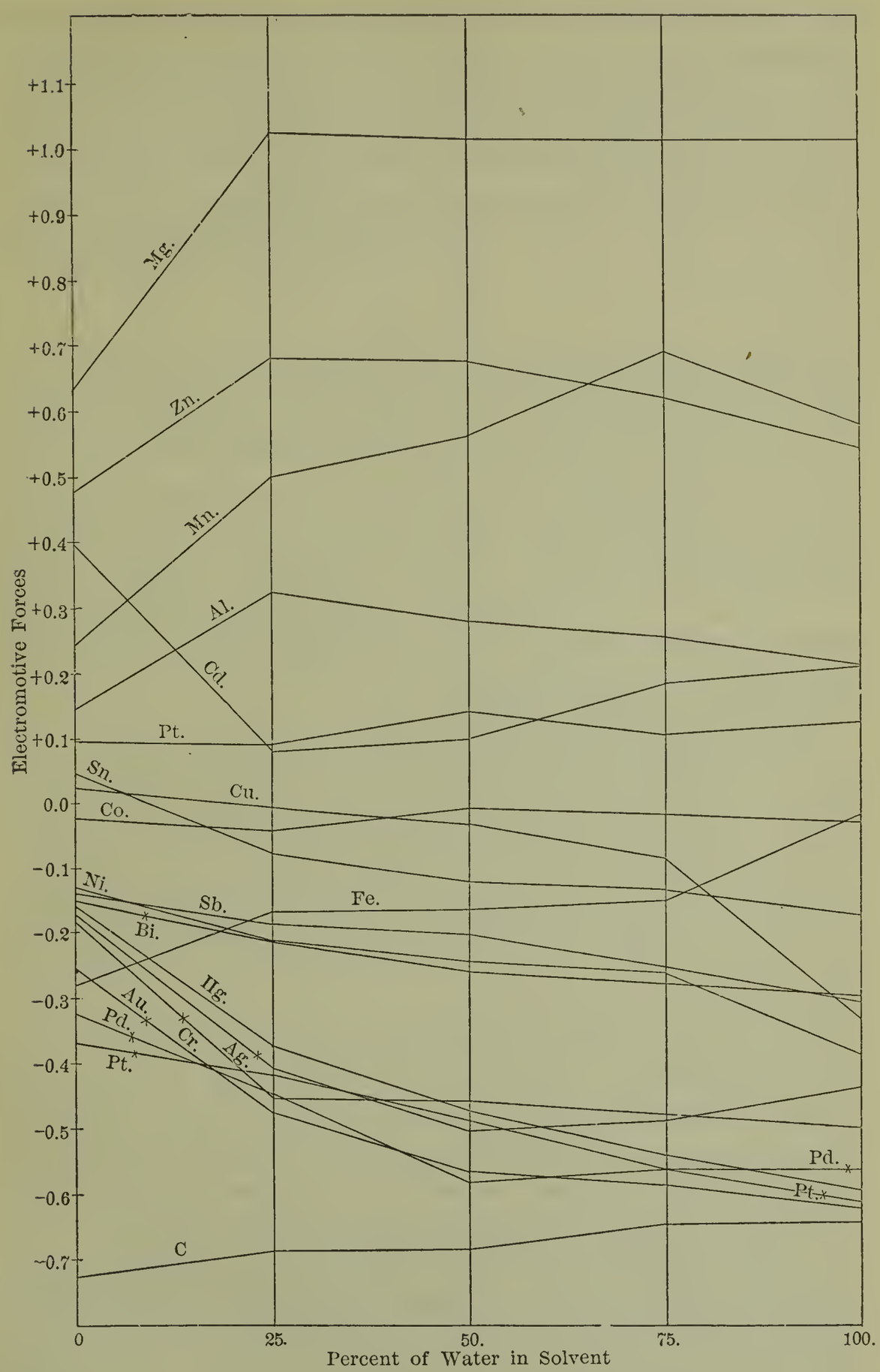


FIG. 1.—DIAGRAM INDICATING EFFECT ON RELATIVE E.M.F. OF VARYING PERCENTAGES OF WATER IN SOLVENT.

the foot, while the other metals suffer great displacements in some cases, and lesser ones in others. The absolute values of the potentials in columns 1 and 5 in Table 7 are in general quite different. In the pyridine solution the potentials are distributed over a smaller range, +0.638 for Mg and —0.374 for Pt or a total difference of 1.012; while in the aqueous solution the difference is + 1.090 for Mg and — 0.611 for Pt, or a difference of 1.704, being a very material difference indeed. This is well brought out graphically in Figure 7.

Toward the noble metals the pyridine solution is more positive than the aqueous solution (compare columns 1 and 5, Table 7). This is on the whole what one would expect considering what is known concerning the affinity which these metals have for the elements of water on the one hand, and for pyridine on the other. Perhaps the most notable displacement of any metal in the series is that of iron. In column 1, Table 7, it stands below gold, whereas in column 5 it is next to lead. A solution of silver nitrate in pyridine may be boiled in contact with iron without precipitating the silver or even tarnishing the iron. This is quite in harmony with the electromotive behavior.

The difference of potential between a metal and a solution may then vary very greatly with a change in the solute as well as with a change in the solvent; and since this variation differs in the case of different metals for one and the same change in the electrolyte, either as to direction or magnitude, or both, the electrochemical series of the metals is frequently subject to relatively very considerable variations, and must not be regarded as something even fairly constant. The work of earlier experimenters, such as Fechner, de la Rive, Faraday and Wheatstone, and in more recent years the measurements of Sylvanus P. Thompson, all of which were made with aqueous solutions, serve to illustrate and to emphasize the same fact. A clear recognition of these changes in the electrochemical series is of great importance in electrochemical practice, particularly in the electrolytic separation of the metals.

A further detailed study of the differences of potential between metals and electrolytes from the stand-point of the chemical affinity existing between the metal and the electrolyte as the determining factor is being made in this laboratory; for though — since Faraday's law holds for all electrolytes as far as known at present — the difference of potential between a metal and an electrolyte is

recognized as a measure of the chemical affinity existing between them, the electromotive forces have not been foreshadowed from the affinities involved. The Helmholtz-Gibbs formula, to be sure, enables one to calculate the electromotive force of a cell from a knowledge of its temperature coefficient and of the thermal changes which accompany the chemical reaction that takes place in the cell when the circuit is closed.

Discussion.

Dr. W. D. Bancroft (Chairman): In deducing the van't Hoff-Raoult formula we remove from the solution a certain amount of the solvent by means of a semipermeable membrane and the assumption is made explicitly that there is no specific affinity between the solvent and the solute under these circumstances. These experiments of Mr. Kahlenberg seem to show that such an affinity does exist, and in that case it seems to me that these experiments throw a good deal of doubt on our present manner of determining molecular weights and solutions—a conclusion of course which does not terrify Mr. Kahlenberg in any respect.

Dr. H. E. Patten: Granting Doctor Kahlenberg's point that we have an affinity beween solvent and solute, this affinity is measurable by the heat of union, and can be converted into volts. While it is true that the e.m.f. varies from solvent to solvent, it can be discussed in terms of the heat of union between the solute and solvent for the particular concentration of electrolyte used. That has not been done here for the very good reason that thermal data are not yet at hand. Of course we are limited by our inability to account adequately for the "bound energy," as Professor T. W. Richards states in his paper on the Relation of the Hypothesis of Compressible Atoms to Electrochemistry, presented yesterday; still much value attaches to discriminating use of heats of reaction and of solution.

For example, the single potential of aluminum against lithium chloride in water is given as + 0.204 volt, and nowhere in Fig. 1 rises above + 0.321 volt. In table I, page 74, Vol. V, Transactions of the American Electrochemical Society, Mr. Mott gives + 1.45 volt as an experimental value for the single potential of aluminum, against aqueous aluminum chloride, derived from the decomposition voltage of aluminum chloride 3.45, as determined between platinum electrodes. The low value given by Doctor Kahlenberg is almost certainly due to a film upon the aluminum. Aluminum gives from 0.8 to 0.65 volt against platinum in aluminum bromide dissolved in ethyl bromide for the total cell; but if a current be passed for a time with the aluminum as cathode and the e.m.f. of the cell then measured, its total voltage is some 2.3 volts, and the true single potential of aluminum against this solution is seen to be + 1.1 volt. Aluminum deposited from this solution shows the same single potential, + 1.1 volt. Under proper conditions, then, it is possible to get the single potential of aluminum fairly well defined.

Prof. LOUIS KAHLENBERG: Concerning the question of semipermeable membranes, I should like to state that during the past year I have given this matter careful attention and have found that osmosis is really due to affinity. Semipermeable membranes, so called, do have affinity for solvents which they permit to pass. In my opinion there is good evidence for assuming that substances dissolve because they have affinity for the solvent and the solvent has affinity for them.

With regard to the remarks of Doctor Patten, I should like to say that he has simply given us his ideas as to how the problem might be investigated further.

As to the single potential of aluminum, it is a well-known fact that the figures ordinarily found in textbooks are quite high. The potential as actually found in practice is usually relatively low, which fact is frequently explained by the assumption that oxide films form on the plate. We might very well consider that the question of the exact potential of aluminum is still a debatable one.

The following papers were read in the absence of the authors by the section secretary.

THE LEAD VOLTAMETER.

BY ANSON G. BETTS AND DR. EDWARD F. KERN.

The voltameters which are employed for measuring the amount of electricity passing through an electric circuit are the silver voltameter, the copper voltameter and the oxy-hydrogen or detonating gas voltameter. These are named in the order of their scientific importance.

Since there is the least possibility of complications occurring in the deposition of silver from a concentrated neutral solution of silver nitrate, due to the monovalency of silver, the results obtained by using the silver voltameter are accepted as the most accurate "This apparatus is universally recognized as the most accurate instrument of its class." (Oettel's "Exercises in Electrochemistry," p. 19.)

Before taking up the experimental part of this paper, a short account of the silver voltameter is given, as it is the standard apparatus with which the lead voltameter was compared.

"The uniform results obtained in the electrolysis of a concentrated neutral solution of silver nitrate have lead to the adoption of the silver voltameter as the standard instrument for measuring electric currents." (Carhart's "University Physics," p. 260.) "It is not employed for currents much larger than 1 ampere, because of the high cost of the material used for constructing the apparatus." For larger currents the copper voltameter is employed.

The results obtained by the use of the copper voltameter are not so uniform as those obtained by the silver voltameter, because the electrochemical equivalent of copper is so small, and also because the weight of copper deposited is a function of the temperature and of the current density at the cathode. But for ordinary current measurements, the copper voltameter is employed, as it has been found that with current densities of 1.5 to 14 amperes per sq. ft. of cathode exposure, the results are fairly accurate, enough so for ordinary experimental purposes, and, besides, it is an inexpensive apparatus.

"The high equivalent weight of silver and the fact that a very considerable quantity of metal is precipitated by comparatively feeble electric currents reduces the error of weighing the deposit to a minimum. The disadvantage which must be recognized in using the silver voltameter is that the silver is greatly inclined to separate as crystals, which are loosely attached to the cathode; consequently, strong currents cannot be sent through the apparatus for any length of time without the possibility of some of the deposited silver becoming detached. The electrolyte recommended is a moderately concentrated neutral solution of silver nitrate, about 15 to 20 grams of pure silver nitrate in 100-cc solution. The anode is a bar of pure silver, wrapped with muslin or filter paper, and the cathode is either a sheet of silver or a platinum dish." (Oettel's "Electrochemical Experiments," p. 38.)

Prof. Barker wrote that "it is evident that the results obtained by using a voltameter for measuring electric currents will be the more accurate in proportion as the electrochemical equivalent of the ion employed is higher." In most precise voltametric work, therefore, the silver voltameter is preferred, since the chemical equivalent weight of silver is 107.93. As a precaution he recommends that "the strength of current which is allowed to pass through the apparatus should not exceed 5 milliamperes per sq. cm cathode surface" (about 5 amperes per sq. ft.). (Barker's "Physics," p. 745.) In practice, however, a current density of 9 amperes per sq. ft. cathode exposure is employed by the Westinghouse Electric Company for calibrating electrical measuring instruments. (*U. of T. Record,* Vol. IV, p. 237.)

Up to within the past two or three years the results obtained by using the silver voltameter were thought to be accurate, but since then a number of experimenters have conducted careful researches for the purpose of finding inaccuracies which are apt to occur in using this apparatus. Several years ago the Reichsanstalt carried out a careful research and found that a source of error in using a silver voltameter was due to too great current density, and also to change of acidity or alkalinity of the electrolyte, caused by secondary reactions at the electrodes. (*Electrochemical Industry,* Vol. I, p. 36.)

Modifications of the silver voltameter have been described by Farup (*Zeit. f. Electro-Chemie,* Aug. 14, 1902) and by T. W. Richards, who found that with the ordinary type of silver voltameter the results obtained were not quite satisfactory. Richards pointed

out that the main trouble arises from the formation of complex ions at the anode, and which, when transported to the cathode, deposits too much silver. This he prevented by using a fine-grained porous cup for the anode compartment. Leduc stated that he hoped to prevent the formation of the disturbing complex ion by having a small current density at the anode. (*Electrochemical Industry,* Vol. II, p. 288.)

In the *Physical Review* of June, 1904, K. E. Guthe describes a series of experiments which he made in order to compare the different forms of silver voltameters. He found that "the usual form of silver voltameter is not a very reliable instrument for measuring quantities of electricity, but that the Richards porous-cup voltameter is the most satisfactory form for the purpose." (*Electrochemical Industry,* Vol. II, p. 288.)

Judging from the results obtained by these able experimenters and by several others, the inaccuracies resulting from using the silver voltameter are very small and for general purposes need not be considered. "The variation of the electrochemical equivalent of silver is from 0.011156, obtained by Mascart, to 0.011195 obtained by Pellat and Leduc. G. Van Dijk and J. Kunst found the mean value of 24 experiments to be 0.0111818, which the authors believe to be accurate to within one part in 10,000." (*Electrochemical Industry,* Vol. II, p. 117.)

For measuring the current for ordinary purposes, such as the calibration of electrical instruments and for finding the electro-efficiency of electro-chemical experiments, such accuracy as mentioned above need not be considered. This extreme accuracy need only be considered in establishing the standard ampere and coulomb, and for comparison in the determination of atomic weights of the metals by electrolysis.

"After all, the silver voltameter with its faults must be considered a standard instrument for measuring electric current until something better has been devised. In the meantime any of the much needed improvements in it will be welcomed." (*Electrochemical Industry,* Vol. I. p. 73.)

It is not the intention of the authors of this paper to try to replace the silver voltameter by the lead voltameter, but to describe the lead voltameter, and show wherein it possesses features which might be a means of its replacing the copper voltameter for technical purposes, such as calibrating electrical instruments and for comparison of electroefficiency of electrochemical methods.

The advantages which the silver voltameter possesses over the copper voltameter are, that the electroequivalent weight of silver is almost three and one-half times as large as that of copper, and that copper forms two compounds, in one of which the valency is twice as great as in the other. Under certain conditions of current density and temperature the copper compound of lower valency is formed, in which case the amount of copper deposited is too great. Silver also gives less trouble than copper, because the plates are less liable to oxidation. For ordinary purposes, however, the copper voltameter is sufficiently accurate, when the requirements as regards current density, temperature and composition of electrolyte are followed. Its general use is due principally to its being inexpensive, and also that the deposit which forms is smooth; so that short-circuiting due to growth of crystals does not occur, which property allows of its being left in the circuit for any length of time.

It has been found that the limits of current density in the copper voltameter are from 0.6 ampere to 14 amperes per sq. ft. (0.06 to 1.5 ampere per sq. dm.) of cathode surface exposure. By keeping within these limits, and by giving due attention to temperature, to composition of electrolyte, and to having good circulation of the electrolyte, the results obtained by its use are sufficiently accurate for general purposes. (Elb's "Electrolytic Preparations," p. 7; Oettel's "Electrochemical Experiments," p. 40.)

A glance at a table of electroequivalent weights of the metals will show that the metals which are deposited as solid metal on the cathode, and which possess high electroequivalent weights are silver (107.93), lead (103.46) and mercury (100.00). The first two metals on account of forming hard solid cathode deposits are well suited for voltameters.

The Lead Voltameter.

We are not aware that lead has ever been employed as a voltameter for measuring electric currents by any one except ourselves. Previous to the invention of the Betts process of refining lead alloys, the crystalline non-adherent deposit which forms on the cathode in the ordinary solutions was not suited for voltametric measurements. One of the claims of the Betts' patent is the formation of a smooth, dense, coherent, solid deposit of lead on the cathode in an acid solution of lead fluosilicate, which contains an organic reducing agent, such as gelatine, glue or pyrogallol, etc. This solution has been used constantly for over two years in the re-

finery at Trail, British Columbia. It is an inexpensive solution, easily prepared, and easily maintained. It conducts the current well, is non-volatile and is stable under electrolysis, which properties make it a suitable electrolyte for a voltameter. It also possesses the property that under ordinary conditions, when a soluble anode is used, no lead peroxide is formed, because the electrical potential required is so low, being in the proximity of 0.18 volt for concentrated solutions and about 0.40 volt for very dilute solutions, when using a current density of 10 to 15 amperes per sq. ft.

Several months ago the lead voltameter was compared by one of us with the copper voltameter, and the results were such that the lead voltameter has since been employed in our laboratory for measuring current efficiencies of electro-chemical experiments.

The results given in this paper are those obtained by comparing the lead voltameter with the silver voltameter.

Experimental Part.

The lead electrolyte was prepared by treating ordinary white quartz with commercial hydrofluoric acid (30 per cent acid) forming a solution of hydro-fluo-silicic acid (H_2SiF_6). Heating the solution of hydrofluoric acid caused more rapid solution of the quartz. White lead (basic lead carbonate) was added to the solution in the required quantity. It dissolved rapidly and completely with effervescence, and any hydrofluoric acid which did not react with the silica formed an insoluble precipitate of lead fluoride, which was filtered off. Lead fluo-silicate is a very soluble salt. It dissolves in about 28 per cent of its weight of water at 20 deg. C. The crystalline salt has the composition $PbSiF_6.4H_2O$.

The solution was diluted so as to contain 17 grams of $PbSiF_6$ and 7 grams of free H_2SiF_6 in 100-cc solution. After adding 1 gram of gelatine (dissolved in hot water) to 2000 cubic cm of solution, the electrolyte was rendered absolutely pure, in respect to metals which can deposit with lead, by electrolysing for several days, using electrodes of refined lead. The anodes were wrapped with two thicknesses of clean linen, so as to prevent the impurities from dropping off and floating in the electrolyte. The small amount of soluble impurities in the electrolyte was due principally to the impurities in the white lead used for making the solution. The electrolysis was continued for four days at temperatures between 17 deg. C. and 57 deg. C. using a cur-

rent density at the electrodes of 10 to 12 amperes per sq. ft. A small amount of "anode sludge" remained behind and in order to prevent it from being oxidized by the atmosphere and subsequently going into solution, melted vaseline was poured on the surface of the electrolyte. The deposit which formed on the cathode was smooth, dense and non-crystalline.

After purifying the electrolyte, about 800 grams of absolutely pure lead was made by electrolysis, using ordinary refined lead, wrapped with clean linen, for the anodes. The refined lead which was deposited on the cathode was further refined by reversing the current and redepositing it on new cathodes. The solution was protected from the atmosphere by a covering of melted vaseline. The purified lead was melted, cast into a thin plate and then rolled into sheets about 1/32 in. to 1/16 in. thick. The sheets were cut into strips of suitable size and used as anodes for the lead voltameter. No residue was left on dissolving the purified anodes by electrolysis.

The silver voltameter, which was used as the standard for comparison, was a glass beaker containing 500 cubic cm of a 15 per cent concentrated neutral solution of silver nitrate. The anodes were four rods of repurified silver, 5/8 in. wide by 3/16 in. thick, and an average length of 4 ins. giving a total active surface exposure of 12 sq. ins. (one side and two edges). The anodes were loosely wrapped with 3 thicknesses of clean linen, serving the double purpose of a porous compartment and to prevent any particles of silver from dropping off. The cathode was a sheet of platinum, having an exposure of 3 ins. x 3 1/2 ins., or a total exposure, both sides, equal to 21 sq. ins. The electrolyte at start and at finish of the experiments was neutral to fresh litmus paper.

The lead electrolyte used for the first series of experiments contained 13 1/2 per cent of lead fluo-silicate ($PbSiF_6$) and 6 1/2 per cent of free hydro-fluo-silicic acid (H_2SiF_6). It was prepared by diluting the purified electrolyte and then precipitating the excess of lead by pure sulphuric acid. The anodes were strips of the purified lead. Two glass beakers, each containing 500 cubic cms of the electrolyte, served as voltameters. (The action of the electrolyte on glass is small and the solution in a short time loses its originally small solvent action on glass. It may be kept in glass bottles.) The two lead voltameters were connected in series with the silver voltameter, and for convenience of approximately determining the current, an ammeter was also placed in the circuit.

TABLE NO. 1.—*Lead Electrolyte Contained* 13.5% $PbSiF_6$ and 6.5% *Free* H_2SiF_6.

A	B	C	D	E	F	G	H	I	J	K	L	M	
Experiment number.	Duration of experiment.	Grams of silver deposited.	Grams of lead deposited.	Grams of lead dissolved.	E.M.F. of silver cell.	E.M.F. of lead cells.	C.D. per sq. ft. of lead cathode.	C.D. per sq. ft. of lead anode.	Calculated amperes from silver deposits.	Calculated amperes from lead deposits.	Percentage error of the lead voltameters.	Calculated electroequivalent weight of lead.	Remarks on the lead voltameters.
1	1½ hr.	5.8958	A5.6221	5.6910	0.36V	0.36V	16.	16.	0.9765	0.9715	—0.512	102.90	One anode and copper cathode.
2	.....	.....	B5.6396	5.7002	.....	0.14V	8.	9	.....	0.9745	—0.205	103.24	Two anodes and lead cathode. Smooth, dense deposits.
3	1½ hr.	5.7863	A5.5246	5.5970	0.36V	0.14V	7.5	8.6	0.9583	0.9547	—0.375	103.04	Two anodes and copper cathode.
4	.....	.....	B5.5450	5.5840	.....	0.36V	15.	15.	.....	0.9582	—0.010	103.43	One anode and lead cathode. Smooth, dense deposits.
5	2 hrs.	7.8408	A7.5108	7.5758	0.36V	0.36V	16.	16.	0.9740	0.9734	—0.062	103.39	One anode and lead cathode.
6	.....	.....	B7.5168	7.5871	.....	0.15V	8.	9.	.....	0.9741	+0.010	103.47	Two anodes and lead cathode. Smooth, dense deposits.
7	2 hrs.	7.6253	A7.3191	7.3693	0.37V	0.37V	15.	15.	0.9472	0.9485	+0.137	103.59	One anode and lead cathode.
8	.....	.....	B7.3221	7.3855	.....	0.15V	7.5	8.5	.....	0.9489	+0.168	103.62	Two anodes and lead cathode. Smooth, dense deposits.
9	1½ hr.	6.2287	A5.9600	6.0404	0.46V	0.16V	8.	9.	1.0316	1.0299	—0.165	103.27	Two anodes and copper cathode.
10	.....	.....	B5.9605	6.0564	.....	0.15V	8.	9.	.....	1.0300	—0.155	103.28	Two anodes and lead cathode. Smooth, dense deposits.
11	4 hrs.	16.6804	A15.9996	16.0720	0.47V	0.14V	8.	9.	1.0360	1.0358	+0.077	103.52	Two anodes and copper cathode.
12	.....	.....	B16.0014	16.0816	.....	0.14V	8.	9.	.....	1.0369	+0.087	103.54	Two anodes and lead cathodes. Smooth, dense deposits.
13	1½ hr.	6.8652	A6.5815	6.6421	0.48V	0.27V	27.	10.	1.1370	1.1373	+0.027	103.47	Two anodes and lead cathode.
14	.....	.....	B6.5812	6.6429	.....	0.27V	27.	10.	.....	1.1372	+0.018	103.46	Two anodes and lead cathode. Smooth, dense deposits, except on lower corners.
15	1½ hr.	9.3253	A8.9590	9.0217	0.64V	0.37V	37.	14.	1.5444	1.5447	+0.019	103.46	Two anodes and lead cathode.
16	.....	.....	B8.9419	9.0114	.....	0.36V	37.	14.	.....	1.5451	+0.045	103.49	Two anodes and lead cathode. Deposit formed very rough and warty on the edges.
17	2 hrs.	6.8566	6.5695	6.6445	0.42V	0.14V	10.	8.	0.8518	0.8514	—0.047	103.41	Two anodes and platinum cathode. Smooth, dense deposit.
18	2 hrs.	6.8754	6.5877	6.7097	0.43V	0.14V	10.	8.	0.8541	0.8538	—0.035	103.41	Two anodes and platinum cathode. Smooth, dense deposit.

TABLE NO. 2.— Lead Electrolyte Contained 8.5% $PbSiF_6$ and 2.5% Free H_2SiF_6.

A	B	C	D	E	F	G	H	I	J	K	L	M	
Experiment number.	Duration of experiment.	Grams of silver deposited.	Grams of lead deposited.	Grams of lead dissolved.	E.M.F. of silver cell.	E.M.F. of lead cells.	C.D. per sq. ft. of lead cathode.	C.D. per sq. ft. of lead anode.	Calculated amperes from silver deposited.	Calculated amperes from lead deposited.	Percentage error of the lead voltameters.	Calculated electroequivalent weight of lead.	Remarks on the lead voltameters.
19	2 hrs.	9.0470	A8.6678	8.7618	0.45V.	0.32V.	9.	10.	1.1238	1.1233	−0.044	103.41	Two anodes and copper cathode.
20	.....	.....	B8.6663	8.7326	.....	0.31V.	9.	10.	.....	1.1232	−0.053	103.39	Two anodes and lead cathode. Smooth, dense deposits.
21	3 hrs.	13.4113	A12.8607	12.9875	0.50V.	0.28V.	9.	10.	1.1107	1.1112	+0.044	103.49	Two anodes and copper cathode.
22	.....	.....	B12.8558	12.9343	.....	0.27V.	9.	10.	.....	1.1107	0.000	103.46	Two anodes and lead cathode. Smooth, dense deposits.
23	2 hrs.	7.2780	A6.9716	7.0313	0.40V.	0.42V.	22.	8.	0.9041	0.9035	−0.066	103.39	Two anodes and lead cathode.
24	.....	.....	B6 9755	7.0272	.....	0.41V.	22.	8.	.....	0.9041	0.000	103.44	Two anodes and lead cathode. Deposit was rough on edges.
25	3 hrs.	7.2738	A6.9695	7.0353	0.30V.	0.38V.	14.5	5.4	0.6024	0.6022	−0.033	103.41	Two anodes and lead cathode.
26	.....	.....	B6.9698	7.0468	.....	0.38V.	14.5	5.4	.....	0.6022	−0.033	103.42	Two anodes and lead cathode. Smooth, dense deposit.
27	2 hrs.	6.5278	6.2550	6.3494	0.41V.	0.24V.	10.	8.	0.8109	0.8107	−0.024	103.42	Two anodes and platinum cathode. Smooth, dense deposit.
28	2 hrs.	6.4864	6.2168	6.2939	0.42V.	0.24V.	10.	8.	0.8058	0.8057	−0.012	103.44	Two anodes and platinum cathode. Smooth, dense deposit.

The electrochemical equivalents of silver and lead which were used are those given by Carl Hering in the *Electrochemical Industry,* Vol. I, p. 170: Silver = 0.001118 grams per coulomb, and lead = 0.0010717 grams per coulomb. Compared with the atomic weight of oxygen = 16.00, the atomic weight of silver = 107.93, and that of lead = 206.92, which gives the electroequivalent weight of lead = 103.46. These values give 4.025 grams of silver and 3.858 grams of lead per ampere hour. The value for silver is that which was adopted by the International Electrical Congress of Chicago, 1893.

Notes.

The three voltameters (one silver and two lead) were arranged side by side and were connected in series. All the electrodes, except the silver anodes, were attached to a strip of hard wood by means of binding-posts. This arrangement allowed all of the electrodes being placed in their respective electrolytes at the same instant, and also being removed and instantly submerged into beakers of distilled water (free from chlorides) which were placed directly back of the voltameters. The cathodes were at once detached from the strip, rinsed with distilled water, then with alcohol, allowed to drain and then carefully dried over a low Bunsen flame. They were placed in a desiccator over sulphuric acid, and as soon as cool were weighed. The lead anodes were washed, dried and weighed in the same manner.

Voltameter A in experiments No. 1, No. 3 and No. 4, and voltameter B in experiment No. 2 contained one anode and one cathode, one side of each exposed to electrolytic action. The size of each electrode was $2\frac{1}{2}$ ins. x $4\frac{1}{2}$ ins.; the surface exposed to electrolytic action was 9 sq. ins. The distance between electrodes was 1 in.

In all the other experiments, 2 anodes and 1 cathode was used. The size of the anodes was $2\frac{1}{4}$ ins. x $4\frac{1}{2}$ ins.; the surface exposed to electrolytic action was 16 sq. ins. The distance between electrodes was 1 in.

The cathodes used in voltameter B in experiments No. 1 and No. 2, and both voltameters in experiments No. 3 and No. 4, were strips of lead, size $2\frac{1}{2}$ ins. x $4\frac{1}{2}$ ins. They were suspended in the electrolyte so that the active surface exposure on one side was $2\frac{1}{2}$ ins. x $3\frac{1}{2}$ ins., or $8\frac{3}{4}$ sq. ins. At the surface of the solution where the lead was exposed to atmospheric action it was slightly etched.

In the other experiments No. 5 to No. 8 and No. 11 to No. 14 the cathodes were exactly $3\frac{1}{2}$ ins. long and were suspended $\frac{1}{4}$ in. below the surface of the electrolyte by a thin strip of metal about $\frac{1}{4}$ in. wide. This arrangement prevented the cathodes from being etched at the surface of the electrolyte where oxidizing action of the atmosphere takes place.

A thin sheet of copper, size $2\frac{1}{2}$ ins. x $3\frac{1}{2}$ ins., was used as cathode in the lead voltameter A in experiments No. 1, No. 2, No. 5, No. 6, No. 11 and No. 12. It was suspended below the surface of the electrolyte by a thin strip of sheet copper $\frac{1}{4}$ in. wide. It was found that there is no action of the electrolyte on the copper so long as it is the cathode and a current is passing. The deposit of lead which formed on it was just as smooth and as dense as that which formed on a strip of lead. This indicates that the copper was not dissolved, which might be expected as copper stands so much lower than lead in e.m.f. series. Copper, however, is dissolved by an acid solution of lead fluo-silicate when the solution containing a piece of metallic copper is allowed to stand exposed to the atmosphere. The only advantage which the copper cathode possessed is that a much thinner strip of metal was used, thereby decreasing the weight, which, when using a delicate balance, was an advantage.

In all the experiments, except voltameter A, experiments No. 1, No. 2, No. 3 and No. 4, two anodes and one cathode were used. This arrangement was found to be the most satisfactory.

The cathodes used for experiments No. 7, No. 8, No. 13 and No. 14 were strips of thin sheet lead, size 1 in. x 3 ins., giving a surface exposure (both sides) of 6 sq. ins., or a current density of 15 to 37 amperes per sq. ft. They were suspended below the surface of the electrolyte by a thin strip of lead 3/16 of an in. wide. The anodes for these experiments were strips of the purified lead size $2\frac{1}{4}$ ins. x $3\frac{1}{2}$ ins., giving a surface exposure of 16 sq. ins.

In experiment No. 8 when a current density of 37 amperes per sq. ft. of cathode exposure was run, the deposit was dense and smooth, except on the edges where it precipitated as small warty formation. These lumps, however, were sufficiently coherent so as not to be detached during washing, drying and weighing the cathode.

When a current of 30 amperes per sq. ft. of cathode exposure is passed through the stronger electrolyte, a smooth dense, non-crystalline deposit formed. A current density of 27 amperes

per sq. ft. was used in experiment No. 7 and the deposit was perfectly smooth and dense; only at the two lower corners was there any inclination to roughness.

An electrolyte containing 8½ per cent of lead fluo-silicate and 2½ per cent of free hydro-fluo-silicic acid (6 per cent SiF_6 and 5 per cent lead) was used for experiments No. 11, No. 12, No. 13, No. 14, No. 15 and No. 16. In all these experiments, except No. 13, the deposit on the cathode was smooth, dense and non-crystalline. In experiment No. 13, when a current density of 22 amperes per sq. ft. of cathode exposure was used, the deposit was smooth and dense, except on the edges where it had a rough warty formation. This shows that the more dilute the electrolyte, the less is the upper limit of current density.

Platinum cylinders, 2 ins. high and 6 ins. circumference, were used as cathodes in the silver voltameter, and in the lead voltameter in experiments No. 9, No. 10, No. 15 and No. 16. The cylinders were flattened, forming a cathode measuring 3 ins. x 2 ins., or a surface exposure of 12 sq. ins. The current used in both the silver and the lead voltameter for these experiments was about 10 amperes per sq. ft.

All the deposits of lead formed in all the experiments, except No. 8 and No. 13, were smooth, dense, coherent and non-crystalline. The deposits were not dissolved from the cathodes, but were formed one on top of the other.

It might be mentioned that the reason for being so particular about purifying the electrolyte previous to the experiments, and for using such pure lead for the anodes was so as to be certain that any variation in the results would not be due to the impurities. Ordinarily, such care need not be exercised in securing such pure lead for the anodes. A good quality of refined lead is sufficiently pure for general purposes.

Conclusions.

The better form of voltameter is one with two anodes and one cathode. Suspend the cathode between the two anodes and below the surface of the electrolyte by means of a thin narrow strip of metal or wire, so as to prevent the action of the atmosphere on the lead at the surface of the electrolyte. This action may also be retarded by using an electrolyte which is less acid than that used in the experiments. Even with an almost neutral

solution of lead fluo-silicate its conductivity would be sufficiently high for a voltameter.

The lead deposit, unlike the silver deposit, is smooth, dense, coherent and non-crystalline. It has a density equal to that of cast lead, so that there is no danger of losing by washing, drying and weighing. The deposit, which forms even with high-current densities (20 to 25 amperes per sq. ft. of cathode exposure in a fairly strong electrolyte) is perfectly smooth, dense and non-crystalline, so long as the electrolyte contains about one part gelatine by weight in two to four thousand parts of solution. With age and by use, the gelatine slowly loses its reducing property. The appearance of the deposit indicates when more gelatine is needed, so that as long as the deposit forms smooth and non-crystalline none need be added. The gelatine is added by dissolving a small quantity in hot water, and adding it directly to the electrolyte. The moment it is added the crystallization of the lead is prevented.

A glance at the tables shows that the current density used within fairly great limits in the lead voltameter does not effect the results. In experiment No. 8 a current density of 37 amperes per sq. ft. was employed, and the results obtained agreed as closely with the silver voltameter as when lower-current densities were used. The limit of the current density seems to be controlled by the strength of the electrolyte and by its circulation. The more dilute the solution the less is the limit of current density which can be used. This is shown by the deposits which formed in experiments No. 7, No. 8, No. 13 and No. 14.

The lead voltameter is well adopted for obtaining electrochemical efficiencies of experiments which require long duration. Lead has the property in common with copper in that the deposit, which forms in some electrolytes, is perfectly smooth, dense and non-crystalline. It, however, possesses some advantage over copper in that the electrochemical equivalent of lead is over three times as great as that of copper.

Of great importance is the fact that while an acid copper sulphate solution in contact with copper electrodes contains varying quantities of cupreous sulphate. Lead exists in the solutions only as divalent ion. On this circumstance is founded our belief that the lead voltameter, properly used, will be found of extreme accuracy.

One advantage of lead over silver is its cheapness, so that with a small outlay a lead voltameter of any size may be constructed.

When necessary this will serve as an apparatus for accurately measuring strong currents of electricity, as much as 100 amperes, and even more, the limit being the size of the apparatus.

From an electrochemical point of view the lead voltameter also has an advantage over the silver voltameter in that lead stands very high in the e.m.f. series, so that the impurities which are ordinarily contained in refined lead will remain as "sludge" on the anode, whereas the purest silver is required for the construction of a silver voltameter.

The table shows that the lead voltameter compares very favorably with the silver voltameter, as the results are within sufficient limit of accuracy for most voltametric work. In the majority of the measurements the electroequivalent weights of the lead are almost theoretical. According to the most recent tables, the atomic weight of lead is 206.92, which makes the electroequivalent weight of lead equal to 103.46. These values in the table were obtained by the simple proportion: (Weight of deposited silver) : (Weight of deposited lead) = 107.93 : x.

The difference in the amounts of lead dissolved from the anodes and deposited at the cathodes show that oxidation of lead took place to a serious extent, particularly when the solution had not had lead electrodes recently immersed in it.

For accurate work we recommend passing a current of pure carbon dioxide through the oxygen-free electrolyte in a covered receptacle. We do not think any further precautions will be necessary in washing and drying than we have used. It will be desirable to use fresh polished cathodes of lead or copper each time rather than redeposit metal on cathodes which have already been used. Should any oxidation of lead during drying take place with the formation of lead oxide, for example, the error caused by dipping such oxidized metal into the acid solution would be increased to 13 times (or the atomic weight of lead 207 divided by that of oxygen 16), the error caused by the simple oxidation.

This paper is far from complete. More work needs to be done in order to develop the possibilities of the lead voltameter, and to find out whether or not it is an accurate instrument. It is possible that it is as accurate as the standard silver voltameter, and for most purposes could be used in its place. It has cheapness and convenience of construction in its favor, as well as the formation of dense, coherent, non-crystalline deposits on the cathode.

CHLORINE IN METALLURGY.

BY JAMES SWINBURNE.

The essence of metallurgy, as practised for thousands of years, is the reduction of the oxide of the coveted metals with carbon, as such or as monoxide. Some metals, notably iron, exist in nature ready as oxide, but most of the others are found as sulphides. The sulphides are, therefore, roasted to convert them into oxides, and the oxides are reduced with carbon. Modern metallurgy broadly consists of the reduction of oxides to the metallic state.

In many cases this process involves very serious difficulties and losses. In smelting iron, the resulting metal is impure, as the ore and fuel contain objectionable elements which come out in the final metal. Zinc oxide needs a high temperature for its reduction, and the volatility of the metal necessitates closed retorts which wear out and leak, so that there is serious loss of metal. Lead sulphide is easily oxidised and reduced without carbon; but the silver present comes out alloyed with the lead; however, its metallurgy is very simple. Copper smelting, though exceedingly simple in broad principle, is excessively complicated in fact, owing to the presence of iron, arsenic, antimony, phosphorus, sulphur, etc., in the ore and fuel.

The smelting by reduction with carbon has, as every process must have, special difficulties of its own with particular ores. A good example is the mixed lead and zinc sulphides, containing silver and gold. Such an ore cannot well be roasted, to begin with, as the oxide of lead fuses and binds the ore into lumps or cakes. Even when it can be roasted, it cannot be smelted as a zinc ore because the lead oxide attacks the retorts. Besides, as an ore yielding zinc only, it may be poor, though the total value of the contents, could they be extracted, are high. Treated as a lead ore the zinc is in the way. Such an ore could only be smelted for lead in the blast furnace, where the zinc volatilises and comes down as oxide and is quite unwelcome. In some cases the zinc and lead can be separated to some extent by concentration. This means

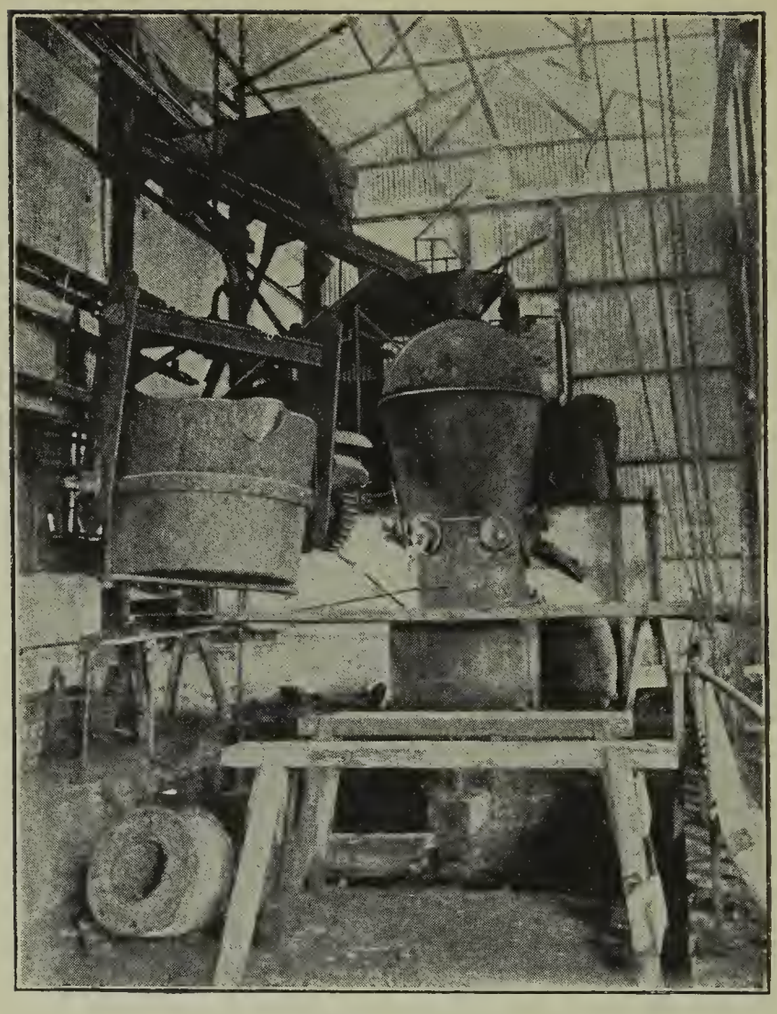


Fig. 1.— Transformer.

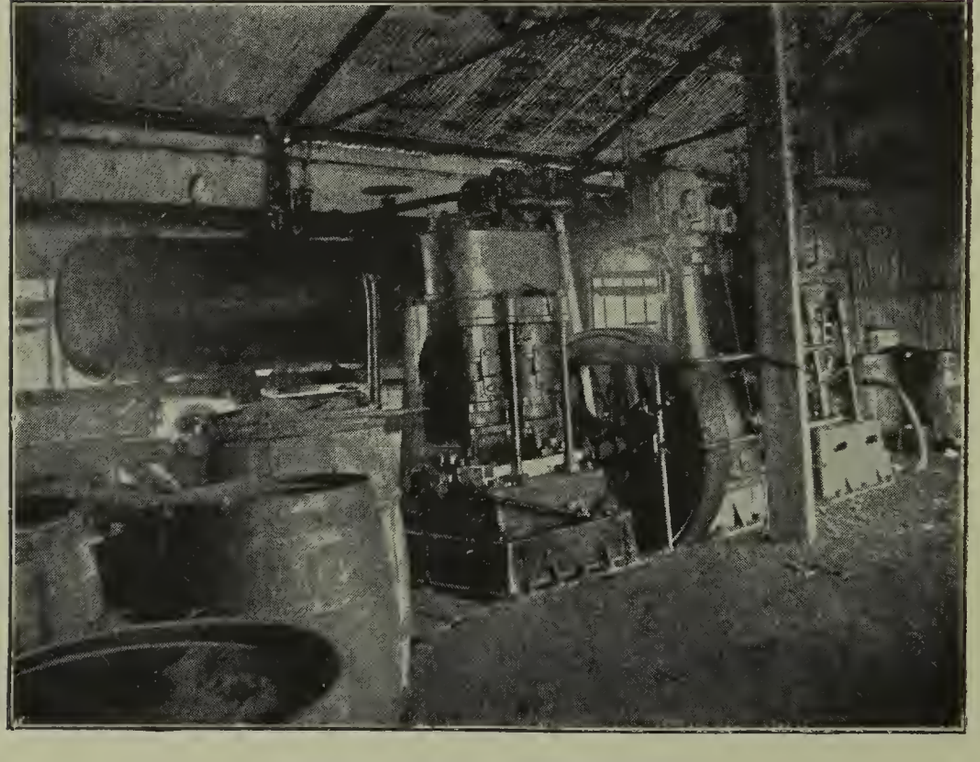


Fig. 2.— Chlorine pumps.

that most of the ore is wasted altogether. Of the rest some is converted into a rich zinc ore contaminated with lead, and some into rich lead ore polluted with zinc. The silver generally prefers to go largely with the zinc. But many of the ores cannot be concentrated, and are at present best left buried.

Another example is antimonial gold. To begin with, there is often not enough stibnite for liquation, so concentration is necessary. But auriferous antimony sulphide is not much used. It can be treated as a simple antimony ore, and the antimony contains the gold, or it might be treated as a gold ore, the antimony being lost; but there is no process in use, as far as I know, which yields both the antimony and the gold separate.

The process I have the honor of bringing before you depends on the action of chlorine. Chlorine has been used in metallurgy before for attacking metallic gold; and salt has been employed for "chloridising" roasting. The present process is, however, a new departure, of quite a different kind, and is really a new form of metallurgy calculated to displace the oxidation and reduction processes now in use to a great extent. How far the replacement will take place depends eventually on economy only.

The principle of the process is treating sulphide ores, without previous roasting, with chlorine, so as to form chlorides of the metals, the sulphur being liberated as such. The chlorides are then electrolysed, yielding metals and recovering the chlorine. The chlorine thus goes round and round; and the process in its simplest form is analogous to separating the sulphur from the metals electrically, or changing the ore, at the mere expense of electrical energy, into its component metals and sulphur. This can in fact be actually done. In one of my first patents there is a description of electrolysing a bath of, for instance, zinc chloride and zinc sulphide with carbon anodes and fused zinc cathode. This gives off zinc at the cathode, and pure sulphur, not chlorine, at the anode. This simple method is not applicable to many ores on account of gangue, iron and other metals. It is mentioned to give a clear idea of the essence of the process.

In practice there are further modifications. The process naturally gives the best commercial return on ores that are refractory to other treatment; and complex ores yield mixtures of chlorides and gangue which could not be electrolysed straight off without intermediate treatment. The intermediate treatment is

always simple chemically, and consists in removing the gangue, and substituting zinc for the other metals one after the other till there is nothing but chloride of zinc left. This chloride of zinc is then electrolysed and the zinc and chlorine recovered. If there was no zinc in the ore, all the zinc obtained is used up again; but if there was zinc in the ore it is sold as zinc.

The action of chlorine on sulphides is generally very vigorous, and enough heat is generated to keep the mass hot. The transformer is something like a small cupola. It is an iron vessel lined with firebrick, and it contains mixed chlorides fused carrying the gangue and ore. The ore is run in at the top continuously and chlorine is pumped in at the bottom; sulphur coming off and passing over into a condensing chamber. There is no difficulty about pumping chlorine. Fig. 2 shows the actual pumps in use. Iron cylinders, pistons and valves are employed, and, as is well known, though not fully realized, dry chlorine, such as that from the electrolysis of fused chlorides, is a very harmless gas.

The transformer is tapped at intervals, and the mixed chloride and gangue run into water. Broken Hill slime, a waste product daily becoming more mountainous, has been chosen to work upon. It contains zinc, lead, iron, silver, manganese, sulphur and gangue. The gangue and lead chloride come out together, and the lead chloride is separated, the silver extracted, and the lead chloride electrolysed. The soluble chlorides are treated with chlorine, to get ferrous into ferric chloride, and the iron precipitated with zinc oxide or calamine. The manganese is got out separately or with the iron in a similar way. The zinc chloride is then boiled down and electrolysed. Fig. 3 shows the evaporating vats, but it is not very clear. The electrolysis vat is simply an iron case lined with fire brick, and is kept hot by the excess of the electric over the chemical energy.

The history of the process is simple. The first patents were in 1897, and the process was tried in the laboratory and everything worked well. It was then tried on a pound scale and worked. A works was taken in Milton, and large scale experiments on electrolysis and handling of chlorine were carried out. A 3,000-ampere electrolytic vat was run continuously for three months. Facilities were wanting there. Mr. A. J. Smith, the general manager of the Castner-Kellner Company, saw a chance of a future in the process, and the company made arrangements for us to put down an ex-

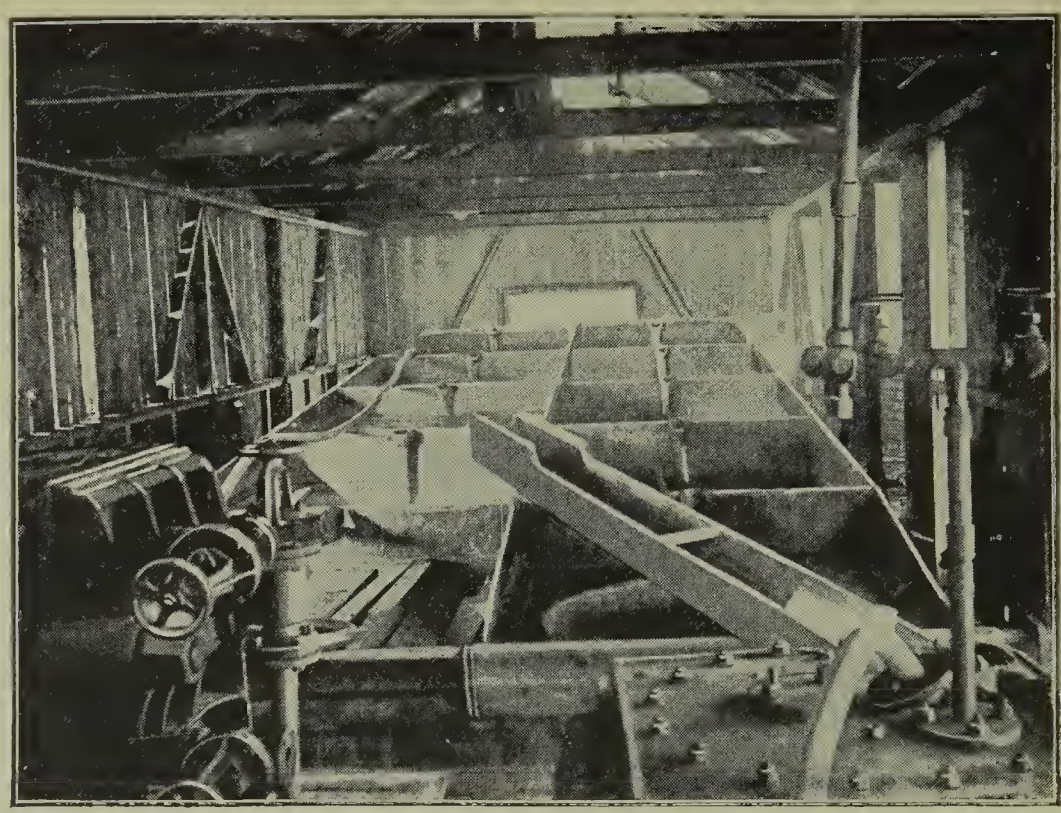


FIG. 3.— EVAPORATING VATS.

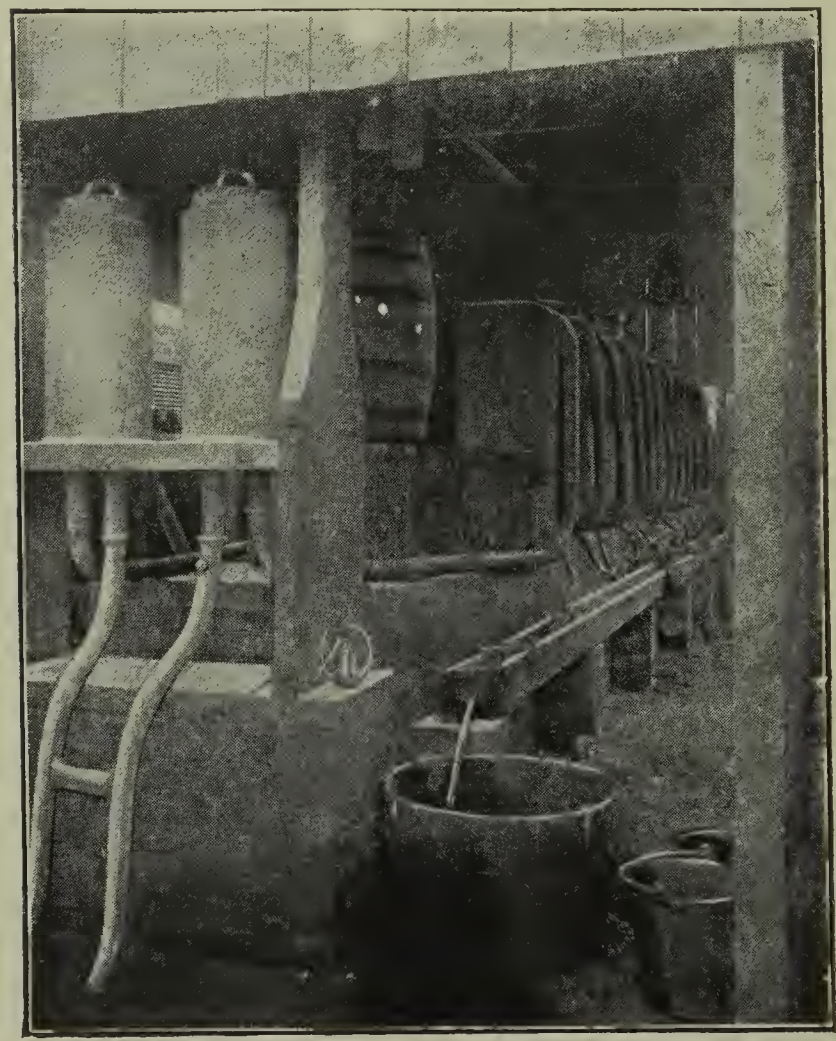


FIG. 4.— DRYING TOWERS.

perimental place next door to their works. This was done and the transforming was proved on a large scale. We have repeatedly learned from the technical journals that the chlorine reaction does not take place, and that fused zinc chloride cannot be electrolysed. In fact people have proved it with test tubes. The Castner-Kellner Company, however, were able to investigate the working of the process, and to inspect the transformer consuming at the rate of 30 tons a week. They were well enough satisfied with the results to arrange to take the works over, acquiring a license to make chloride of zinc. They thus use the whole process except the electrolysis, as they have a supply of chlorine from the soda works. They will run a 10,000-ampere vat for demonstration, but otherwise they will sell every metal but zinc, the zinc being sold as chloride. The only difference in the process is that zinc chloride must be much more highly refined for the market than for electrolysis, as a trace of manganese, for example, would spoil the color, but would do no harm in electrolysis. The chlorine is also damp, and has to be dried before being pumped.

Fig. 4 shows the drying towers. They contain zinc chloride. The Castner-Kellner Company are reorganizing the works, and reconstructing it in many details, and will probably have the first unit, dealing with 30 tons of ore a week, running this fall.

It is of little use repeating in one paper what is already accessible elsewhere. I have gone into much greater detail in a paper before the Faraday Society, June 30, 1903. This paper gives rough approximations as to profits, costs, and explains which ores can be treated and which cannot. I must also refer to a paper by Mr. Ashcroft (*Trans.* Inst. Min. & Met. Vol. IX), who joined in 1898 and collaborated with me up to last year, working out the practical development of the process.

A good deal of work has been done recently on the treatment of ores with little metal content, such as copper ores running under 3 per cent, and copper nickel and cobalt ores. These modifications have only been tried on the small scale, and so it is too soon to speak yet, but apparently low grade copper, and nickel, cobalt and of course their mixtures, and copper zinc ores of low content will prove amenable. Such interesting puzzles as the treatment of speiss from copper smelting works, and the smelting of antimony gold ores, have already yielded satisfactory solutions on the small scale, and fahlerz of various compositions is likely to be amenable to simple and profitable treatment.

Discussion.

Prof. W. D. Bancroft (Chairman): The most interesting part of this paper seems to be that on the commercial scale there is no electrochemistry involved; that is, the process works well if that is eliminated, and is successful because the Castner-Kellner Co. has a large excess of chlorine for which it has no market, and thus makes zinc chloride. The case cited hardly proves the actual value of the process in ordinary metallurgical work, because it would hardly be feasible, so far as one can judge, to make caustic soda by electrolysis of salt in every place in which it was desired to use the process.

Mr. S. S. Sadtler: The process mentioned seems to be quite simple. Some may remember seeing the process very completely described in a copy of the *Engineering and Mining Journal.* A half-page was devoted to diagrams showing the different steps, and it seemed more complicated than shown here.

Professor Bancroft: All the metals have to be removed by filtration from fused anhydrous zinc chloride. This must present serious difficulties, but it is said that this problem has been solved.

On motion, the Section then adjourned.

ALUMINOTHERMICS.

BY DR. HANS GOLDSCHMIDT.

A new means of creating high temperature is apt to lay the foundation for more or less important industrial developments. Legends tell us that there was once a time when humanity existed without fire until Prometheus brought the divine fire to the dwellers of the earth and thereby laid the foundation for civilization. In making a step forward across thousands of years, look at the industries before the employment of black coal — before it became known that coal was combustible matter. We perceive that our whole modern technical knowledge is based on the creation of heat by the combustion of black coal. A new fire was supplied by Volta in the electric arc, but it took centuries before the invention of dynamos enabled us to utilize the heat power supplied by electricity, by means of the electric lamps and furnace. We perceive that the fundamental idea and the mere production of heat do not by themselves supply practical results, and that it is only the application that determines the real value, which it sometimes takes many years to detect. To these known means for the production of high temperatures, a new one is now added — the so-called "thermit process."

Although I may assume that most of you know the principles of the process, you will nevertheless permit a short explanation of its essential points. Just as generations passed mineral coal without detecting its combustible properties, it was not known heretofore that aluminum belonged to the combustible products, which under certain circumstances, once ignited, continues its own combustion. Aluminum in a divided state only wants to be mixed in certain proportions with a chemical compound containing oxygen, so-called "oxide," for instance — oxide of iron — in order to obtain a heating compound now known as *thermit*, which name is copyrighted.

It is self-evident that the technical details of its preparations required special study, just as much as the preparation of gunpowder or dynamite. The particular character of this burning thermit is quite different from that of explosives, the effect of which is always

based on instantaneous production of great masses of gas. No gas whatever is produced by thermit. The mass continues the combustion within itself without a supply of air or heat from outside. The chemical reaction is of the simplest, so that the first chemical lesson might commence with an explanation of these simple phenomena. Even to a layman they are quite intelligible, as only three elements intercommunicate. First, aluminum, which is mixed, secondly, with a combination of metal — for instance, iron — and thirdly, oxygen, which combination is called "oxide of iron." If this thermit compound is ignited, nothing except a separation of the oxygen from the iron and a chemical combination with the aluminum results, forming, therefore, aluminum oxide, and setting free or melting out the iron.

When thermit has been burnt down in a crucible, the aluminum oxide, also called "corundum," floats on the top as a slag; the iron lies at the bottom as a regulus.

I have not yet mentioned the most remarkable and important properties of thermit: Firstly, its high combustion temperature, about equal to that of the electric arc — say 3000 deg. C.— and secondly, the speed of the reaction. A density of energy of the heat supply is produced, which has up to the present time never been obtained by other means — not even by the largest electric furnaces hitherto constructed. In this lies the principal reason of the utilization of thermit. Independently from the quantity brought to reaction, the duration of the combustion in the crucible remains about unchanged, say from one-half to one minute. This is explained by the speed of the reaction peculiar to thermit. In a large crucible a large melting zone is formed, which again on the large surface speedily ignites the surrounding particles. Thermit must be ignited by a so-called "ignition powder" of low-ignition point, but producing a high temperature, which in its turn ignites the thermit, as the latter is very difficult to ignite and in consequence presents no fire risk. Thermit thrown into an open hearth fire will not burn, because the temperature of this fire is insufficient to ignite thermit.

Two parts of weight of thermit give one part of pure, mild, malleable iron. If 200 kilograms of thermit are ignited in one crucible, hardly a minute afterward one has at his disposal 100 kilograms of liquid, superheated, mild steel. By no other known means has it hitherto been possible to produce liquid steel in so speedy and simple a manner. No apparatus is required. A crucible lined with highly-

refractory basic material, such as magnesia, is all that is required. If it were desired to obtain the same heat efficiency, about 200 horsepower would be required during one hour. It is easy to understand from this fact the very peculiar heat source with which thermit supplies us. Out of these properties of thermit, we can deduce its applications.

As already mentioned, the development, but more still the introduction, was the work of years. Although the practical application of the process has already made strides, nevertheless, infinite possibilities of new developments will present themselves. I can only mention here the most important ones and only partly touch on some of these, as thermit finds uses in a great variety of applications. The principal branches are the following:

1). Metallurgical applications:
   a). Production of pure carbonless metals and alloys.
   b). Applications in iron and steel foundry practice.
2). Utilization of the aluminogenetic slag, corundum, so-called corubin:
   a). For grinding purposes.
   b). For ceramics in the process of Dr. Buchner, Mannheim.
3). Hard soldering, applications of "sinter" thermit.
4). Welding process.
   a). Pipe welding.
   b). Rail welding.
      i). Embedded trolley rails.
      ii). Exposed T-rails.
      iii). Third rails.
   c). Application of thermit or thermit steel for repairs of all sorts; in particular for maritime repairs and spare castings wanted in a hurry, welding broken bosses of rolls, etc.
5. Application for cooking for camp use.

As above mentioned thermit separates pure metals from their oxides — not only iron, but also chromium, manganese, ferro-titanium, ferro-vanadium, and many others. In this way processes were elaborated to produce on a large scale carbonless metals of a purity not hitherto obtained. A long-standing wish of metallurgists was fulfilled, which electricians could not satisfy in their furnaces, in spite of long-continued studies. The metallurgists now pro-

ceeded to apply these pure metals in practice. Their successful studies on this subject cannot be sufficiently appreciated.

Chromium has first attracted particular attention, and American works are using it in considerable quantities, particularly in the manufacture of high-speed tool steels, whose efficiency is proved by turnings of the thickness of a finger. The usual addition is about 6 per cent chromium besides tungsten, and the carbon contents must be kept as low as possible. For projectiles, carbonless chromium is also used — in short, anywhere that chromium steel of accurate composition is required.

In nearly the same quantities pure manganese free from carbon is used, principally for alloying with copper, besides for the casting of nickel and bronze. It is much used for propellers, which must not contain iron, a condition which precludes the use of ferro-manganese.

Lately molybdenum and ferro-vanadium have been placed on the market. Ferro-titanium has been used regularly for several years by some steel works. This ferro-titanium is introduced into liquid cast-iron in the ladle, by means of the so-called box reaction. In this way highly-heated ferro-titanium is separated out at the bottom of the ladle, which alloys in *statu nascendi* with the contents of liquid iron. The reaction taking place in the midst of the bath, the latter is more thoroughly stirred or poled than is possible by other means. Through the introduction of a small quantity of titanium, which binds the nitrogen, the composition of the bath undergoes a chemical improvement. Impurities, such as slag and others, are driven up, and the bath is further purified.

It is remarkable that the sulphur contents are appreciably reduced. I will mention two analyses.

Cast-Iron.	Before Ti. addition.	After Ti. addition.
No. I.	Mn. 0.36	Mn. 0.30
	S. 0.19	S. 0.09
	Ti.	Traces.
	Before Ti. addition.	After Ti. addition.
No. II.	Mn. 0.66	Mn. 0.64
	S. 0.09	S. 0.07
	Ti.	Traces.

Of late the contents of the boxes are pressed into solid moulds, preventing the possibility of their getting unmixed and producing a

prefectly regular reaction. The iron becomes considerably more fluid and it can, therefore, be cast at a lower temperature and will show very much less tendency to form shrink cavities. The process has been introduced in the course of the last year in a number of foundries, in particular for cylinder castings, high pressure valves, etc.

The possibility of reviving liquid iron or steel locally by this "box reaction" has led to a further application, which has become very important for foundry purposes. In casting steel ingots of more than 10 tons, the piping which occurs in the head and which extends through the upper third of the block causes a great deal of trouble. A box containing from 10 to 20 pounds of thermit, according to the size of the ingot, is introduced just as late as the hardening of the surface will allow its insertion. The reaction will revive the steel in the head and allow the piping to be filled up with fresh steel.

A still more extensive use of box reaction consists of the introduction of thermit into the risers. Formerly a small can of suitable shape was built into the bottom of the risers. Then it was thought a simplification to insert the box at the end of a rod, into the liquid iron, as it rose. Now, in a number of works, the thermit is simply wrapped in paper and thrown on the rising liquid metal. This process is equally applied in the iron and steel casting practice. For cast-iron the wrapper should contain, at the bottom, a pinch of ignition powder, as the temperature of liquid cast-iron is insufficient to start the thermit ignition. Liquid steel does not require ignition powder. Many faulty castings will be avoided by this application.

Having shortly touched on the metallurgical aspect of aluminothermics, before proceeding I wish to mention the uses of corundum slag. This artificial corundum, so-called "corubin" (registered trade-mark), is very different from those of the natural product, and its properties are much more valuable. The cause is the chemical composition of the two materials. The natural product contains various impurities, such as oxide of iron, silica — even small quantities of water in chemical combination. On the other hand, the aluminogenetic corundum is nearly free from all these, and in particular absolutely free from water. This is no doubt the cause of its greater hardness compared to the natural product. In consequence, corubin is used for emery wheels.

The most curious, and in a way, epoch-making application is

one of a colleague of mine, Dr. Buchner, of Mannheim. He found that this material had an exceedingly low elastic coefficient and does not lose this property when mixed with a fire-clay binder. In this way he managed to produce vessels for chemical purposes of entirely different properties than the earthenware vessels in use up to the present. You know how easily a porcelain or earthen vessel cracks when exposed to even small changes of temperature. Those made of corubin behave differently. They can be heated to red heat and cooled suddenly with water without showing any tendency to crack. For instance, for hot muriatic acid only enameled vessels could heretofore be used, which were not reliable and of very limited usefulness. Corubin offers, therefore, almost unlimited advantages to the chemical industry. Its highly-refractory qualities have introduced it as a coating for bricks and tubes exposed to high temperatures. For these purposes only the corubin resulting from the chromium reaction is utilized, of which sufficient quantities are available, in consequence of the large consumption of pure carbonless chromium. This corubin requires a special preparation before being used. The aluminogenetic corubin has proved itself a valuable product for making crucibles for the thermit welding process. Such crucibles, made according to a certain receipt, will stand from 50 to sometimes 100 reactions.

The aluminogenetic welding process, which I shall now deal with, offered this peculiar difficulty. A new fire had been discovered, over which one had not as yet gained entire control. It is a peculiar fire, which is solid and without flame, and which gives half its weight in the form of liquid metal and the other half in the form of overheated slag. In the first experiment, iron rods were steeped into the liquid fire, in order to heat them like in a smith's hearth. Then a thermit was produced which did not liquefy, but only sintered and produced white heat. This, however, showed itself more applicable to hard soldering and less to welding. For the former application it is more handy than a charcoal fire or gas. For welding purposes a different process was found. The pieces were butted between clamps, a mould put around the joint and into this the liquid mass was poured over the top of a crucible. After obtaining welding heat, the clamps were tightened. It was determined by experiments what quantity was necessary for each section and the results were tabulated.

The process, of course, does not claim to replace the smith's fire, but to supply its place where the smith's fire would be insufficient. For instance, it has proved itself very valuable in welding lengths of pipes in installing whole systems. It competes successfully with flanged joints, particularly where the pipe system is used to carry fluids or gases which easily destroy their packings; especially for oils, alkalies, acetylene, and refrigerators; naturally also for high-pressure systems of all kinds. The welded joint is fully as strong as the pipe itself. Recently the manner of welding pipes into "T" shapes has been worked out. It required some little practice to successfully handle the material, but as it obviates keeping a large stock of various sized "T" pieces, it is of considerable importance, especially in outlying districts, mines, etc. The action of the liquid in running out over the lip of the crucible, on to the piece to be welded, is peculiar. The slag corubin flows out first. This solidifies instantaneously on the metallic surface, so that the thermit steel which follows and does not liquefy the thin layer of slag does not touch the welding surface and, therefore, cannot burn through the wall of the pipe. If the aluminogenetic iron were to come in contact with the metallic piece, it would fuse with it. After the weld is made, the slag and thermit can, therefore, be easily removed with a hammer and the welded joint does not require machining.

I now come to one of the principal applications of the process — the welding of rails. The track of a street railway, in consequence of the bed on which it lies and the way in which the rails are held in the pavement, has to be considered from a different point of view than the exposed track of a steam road. The former, at present, has received more attention. Even laymen may know that there are hundreds of mechanical joints, none of which have given entire satisfaction. The demand of engineers for a really continuous rail, that is to say, having everywhere practically the same section, and undergoing in all parts the same amount of wear and tear, is justified. For electric railways using the rails for conducting the return current, this is an additional advantage. Copper bonds are only an imperfect conductor of electricity, because, although when new and well fixed, they give satisfaction, still, in course of time, the skin resistance increases so much that the bonds require renewal. Otherwise the so-called "electrolysis" would take place, causing not only leakage of current, but inter-

ruption in gas and water pipes. These, on account of the large extent of the electric systems in the United States, have received more attention and study here than abroad. A weld offers, of course, the greatest security for efficient conductivity.

To come to the practical side, the first welds were made about four years ago, in the same manner which I described when talking of the welding of pipes. The crucible was emptied by pouring over the lip; the rail ends brought by this means to welding heat were forced together by a strong pair of clamps, so that the section was completely butt-welded. Afterward the process was considerably simplified by, in a way, reversing it and letting the thermit iron run out first, followed by the corundum. Over the mould is placed a conical crucible, plugged in the manner customary in our process. As soon as the charge in the crucible is burned down, it is tapped from the bottom and the iron runs into the mould made of refractory material. The highly-overheated thermit steel fuses with the foot and web of the rails to one homogeneous mass, thus forming an immovable solid shoe. On account of the high temperature, a few pounds are sufficient; the diameter of section is, therefore, only slightly increased, an advantage which is essential. The heat of the corundum that follows is utilized at the same time to bring the heads of the rail to welding heat. In this way the section is heated equally all over, which is material, to avoid bending of the rails. They will remain in absolutely the same position as when put down before welding and are not held by special clamps or bolts. With new rails and under special conditions, a butt-weld is sometimes demanded. This can be obtained by placing the rail ends into a strong pair of clamps. With well-imbedded rails, and especially where they are anchored, a butt-weld is superfluous. With old rails, the life of which can be considerably lengthened by welding, the use of clamps is impracticable.

I wish to give some details regarding the strength of the welded rail. It is about 80 to 100 per cent of the rail itself; you will admit this is a very satisfactory result. The resistance of a butt-welded and not butt-welded rail to vertical pressure from above is about the same. The resistance to pressure will not, however, satisfy critics as long as it is to be feared that the heads of the rail might get softer through having been brought to welding heat, and develop the well-known hollows at the rail ends. This objection must be treated quite seriously, as all the advantages of the process would be of no avail against such a fault. As a matter of fact,

the weld undergoes no change of this or any other sort. The Great Berlin Street Railway has had joints in service for two years and after more than three-quarters of a million cars, not counting the very numerous trailers, had passed over them. The head has remained perfectly level and even with the use of a ruler no unevenness is discovered. This fact disposes most effectually of all fears. Any one can have this fact confirmed, if of two rails of identical material he will have one treated with thermit and then have test-rods cut out of both. Tensile strength and elasticity will be found equal and unchanged. Theoretical explanations can be easily adduced and have been confirmed by the highest authorities. As the operation takes place without the air having access to the welding zone, a chemical change such as would occur in a coal or gas fire is impossible. As in this country there has been as yet no opportunity to meet this objection by practical proof, I may mention the reply I received from a prominent German street railway engineer to my request for small plaster casts of thermit-welded joints that had been in the ground for more than three years. He said he failed to see the object of such casts, as it was well known that the joint would not show any difference from any other part of the surface of the rail. While two years ago only 3000 joints were welded, last year the number reached 20,000, which has already been exceeded in the first half of the present year.

In this country it was only possible to begin the exploitation of the process quite recently, as in consequence of the custom duties it had been found impossible to import thermit from abroad.

Regarding welds of exposed "T" rails, few experiences are at present available. The first practical tests were made this summer at Budapest, on behalf of the Hungarian Government Railway. Lengths of 72 meters, about 240 ft., and even one length of 150 meters — about 500 ft.— were welded together. The tests are being continued at the present moment on other railroads.

A special rail joint calling for remark is that of the third rail. The copper bond in this case is also unsatisfactory, particularly as sometimes very strong currents have to pass through it. Besides, it lies exposed and, therefore, offers great temptation to thieves. In many cases it is sufficient to weld a small bond of thermit steel between the two feet of the rail. A piece of tubing is placed over the mould and charged with thermit. This is ignited and burns down by itself without a crucible being used. The price of such

bonds is much below that of copper bonds. In this way, for instance, a suburban track 13½ miles in length was welded and has stood the test of one winter's low temperature. The joint is mechanically strengthened by one fish-plate on the side opposite to the bond. The Metropolitan Underground Railway of Paris, France, has welded about 20 miles of third rail; in this case the whole section was welded and, of course, no fish-plates were used.

Thermit, however, is by no means used only for small welds, such as rails and tubes. By the possibility of burning down the largest quantities of thermit and of obtaining at a moment's notice any quantity of liquid steel, the process is particularly useful for the largest weld, such as are necessary in ship repairs. A broken stern post, a cracked crank-shaft, can be welded without removing it from its bearings. The results obtained can be appreciated from a number of lantern slide pictures which I shall have the pleasure of showing you at the end of the lecture.

In the Russian-Japanese war thermit has played an important part, particularly on the Russian side. After the first attack of the Japanese on the Port Arthur fleet, orders for several tons were received from the Russian Government. These orders have continued to increase ever since. The remarkably speedy repairs of Russian ships are, according to accounts received by me, in many cases due to thermit welds. The Japanese have, of course, also used thermit, but as before the war it was less known there than in Russia, its possibilities have not received the same attention. Of course some practical experience is imperative before large quantities of thermit can be successfully handled. This experience is, however, not difficult to acquire. In far-off countries thermit has come into constant use, although no experienced mechanics were available, and the engineers had to teach themselves by closely observing the rules laid down in the pamphlets. Of course it is just in such countries where machinery is difficult to obtain that thermit is of inestimable value. By its help urgent spare castings can be made at once out of thermit steel; for instance, cog-wheels.

For a special sort of repair it is used in rolling-mills for welding bosses on rolls. The surface on which the new boss is to be welded is brought to fusion heat by first pouring a little liquid iron on it, which is covered by a quantity of thermit. The latter is ignited and enables the liquid metal which is then poured on it to evenly weld to the roll.

In conclusion, I will mention an entirely novel application. In consequence of a suggestion of mine, the "Deutsche Munitions & Waffenfabrik," Karlsruhe, has constructed a very handy cooking and roasting stove, allowing a speedy warming of food and drink in the open air, by means of thermit, without a flame. This can be of great value in campaigning — for instance, on outpost duty where cooking may be done without divulging one's position to the enemy. To avoid misunderstanding, I may as well mention at once that thermit cannot be adapted for fuel on a large scale, for instance, on torpedo or other boats. In this respect it cannot compete with anthracite, as 1 kilogram of thermit gives about 450 calories, while anthracite gives about 7000. The value of the new heat producer lies in the speed of the combustion and the enormous heat developed, or, as I said at the beginning, its density of energy, not in the great number of available calories. For heating purposes in the ordinary sense, it can, therefore, only be utilized on a small scale, for very specific purposes and where, besides, a particularly low price is not of importance. In such cases the ordinary heat producers cannot be employed with economical results, while thermit, under such conditions, is burnt as in a calorimeter and can be utilized almost quantitatively.

"The new fire" in the short time of its existence has obtained a quite appreciable introduction, but only the initial work has been done, and the present field of its usefulness — in particular for rail-welding purposes — will increase enormously. In the course of time new fields of utility will be discovered for a process which produces in so simple and speedy a manner, without bulky equipment, such enormous temperatures.

THURSDAY, SEPTEMBER 15, 1904.

Joint Session of Section C with the American Electrochemical Society, Thursday, September 15, 1904.

Chairman Carhart called the Section together at 9:30 o'clock.
The following paper was read by the author.

THE SILVER VOLTAMETER.

BY DR. K. E. GUTHE.

1. According to Faraday's law of electrolysis, a strict proportionality exists between the quantity of electricity passing through an electrolyte and the electro-chemical reaction produced by it. The latter may, therefore, serve for the measurement of quantity of electricity. We call the instruments employed for this purpose "voltameters" though the name "coulometers" proposed by Richards seems to be a far more appropriate one.

A good many different types of voltameters have been used, for example, the gas voltameter, in which the volume of the liberated gases is measured, or the iodine and the iron voltameters in which the electro-chemical change is measured by titration. The usual method, however, is the determination of the weight of a substance deposited at one of the electrodes by an electric current[1]. Of the last the copper voltameter and the silver voltameter are the best known types.

The investigations of F. and W. Kohlrausch[2], Rayleigh and Sidgwick[3], Gray[4], Schuster and Crossley,[5] and Glazebrook and Skinner[6] have proved that the silver voltameter is by far the most reliable instrument of this sort and that it will give results accurate to 1 in 5000, if certain specifications as to its construction and treatment are closely followed.

2. This led to the adoption of the silver voltameter as a standard for the measurement of electric current by the International Electrical Congress held at Chicago in 1893. Though the ampere was defined as one-tenth of the unit of current of the c.g.s. system of

1. A description of some unusual types is given by Danneel, *Zeit. f. Electroch.*, vol. 4, p. 154, 1897.
2. Fr. and W. Kohlrausch, *Wied. Ann.*, vol. 27, p. 1, 1886.
3. Rayleigh and Sidgwick, *Phil. Trans.*, vol. 175, p. 111, 1884.
4. Gray, *Phil. Mag.*, vol. 22, p. 389, 1886.
5. Schuster and Crossley, *Proc.* Roy. Soc., vol. 50, p. 344, 1892.
6. Glazebrook and Skinner, *Phil. Trans.*, vol. 183, p. 567, 1892.

electromagnetic units, it was added, that it "is represented sufficiently well for practical use by the unvarying current which when passed through a solution of nitrate of silver in water in accordance with standard specifications, deposits silver at the rate of 0.001118 gram per second." This value is called the electrochemical equivalent of silver.

The specifications referred to above were prepared by the National Academy of Sciences and legalized in the United States in 1894. They read as follows:

In employing the silver voltameter to measure currents of about one ampere. the following arrangements shall be adopted:

The kathode on which the silver is to be deposited shall take the form of a platinum bowl not less than 10 cms in diameter, and from 4 to 5 cms in depth.

The anode shall be a disc or plate of pure silver some 30 sq. cms in area and 2 or 3 mms in thickness.

This shall be supported horizontally in the liquid near the top of the solution by a silver rod riveted through its center. To prevent the disintegrated silver which is formed on the anode from falling upon the kathode, the anode shall be wrapped around with pure filter paper, secured at the back by suitable folding.

The liquid shall consist of a neutral solution of pure silver nitrate, containing about 15 parts by weight of the nitrate to 85 parts of water.

The resistance of the voltameter changes somewhat as the current passes. To prevent these changes having too great an effect on the current, some resistance besides that of the voltameter should be inserted in the circuit. The total metallic resistance of the circuit should not be less than 10 ohms.

Method of making a measurement.—The platinum bowl is to be washed consecutively with nitric acid, distilled water and absolute alcohol; it is then to be dried at 160 deg. C., and left to cool in a desiccator. When thoroughly cool it is to be weighed carefully.

It is to be nearly filled with the solution and connected to the rest of the circuit by being placed on a clean insulated copper support to which a binding screw is attached.

The anode is then to be immersed in the solution so as to be well covered by it and supported in that position; the connections to the rest of the circuit are then to be made.

Contact is to be made at the key, noting the time. The current is to be allowed to pass for not less than half an hour, and the time of breaking contact observed.

The solution is now to be removed from the bowl and the deposit washed with distilled water and left to soak for at least six hours. It is then to be rinsed successively with distilled water and absolute alcohol and dried in a hot-air bath at a temperature of about 160 deg. C. After cooling in a desiccator it is to be weighed again. The gain in mass gives the silver deposited.

To find the time average of the current in amperes, this mass, expressed in grams, must be divided by the number of seconds during which the current has passed and by 0.001118.

In determining the constant of an instrument by this method, the current should be kept as nearly uniform as possible and the readings of the instrument observed at frequent intervals of time. These observations give a curve from which the reading corresponding to the mean

current (time-average of the current) can be found. The current, as calculated from the voltameter results, corresponds to this reading.

The current used in this experiment must be obtained from a battery and not from a dynamo, especially when the instrument to be calibrated is an electrodynamometer."

Other countries in which the silver voltameter has been legalized have adopted similar rules.[7]

3. The minute description of the form and the treatment of the silver voltameter shows clearly that a slight departure from them may result in a deposit of silver not in accordance with the definition of the ampere. It was apparent that there are in the instrument disturbing factors, which required a further study. Kahle[8] has shown that the electrolyte becomes acid by electrolysis and that on repeated use the deposits are too large.

The Reichsanstalt recommends therefore that not more than 3 grams of silver should be deposited from 100 ccm of the solution.

Leduc[9] hopes to overcome all trouble by employing a large silver anode, consisting of granulated silver. He keeps the anodic current density below 0.02 ampere/cm^2 and recommends that the amount of silver collected at the kathode should be large, say about 30 grams.

Patterson and Guthe[10] obtained concordant results by keeping the solution in contact with silver oxide. Leduc speaks in favor of this method, but Richards' results with the same type show great variations in the amount of silver deposited by the same quantity of electricity.

The greatest advance in our knowledge of the subject is due to the excellent researches of Richards[11] and his students, who showed that the main difficulty lies in the formation of a heavy anode solution, containing a complex silver ion, the existence of which had already been suggested by Rodger and Watson.[12] The anode solution which in the ordinary type of voltameter sinks to the bottom of the vessel, producing there a star-shaped figure,[13] will yield on electrolysis more silver than corresponds to the

7. *The Electrician*, vol. 27, p. 325, 1891. *Zeit. f. Instr.*, vol. 21, p. 180, 1901.
8. Kahle, *Zeit. f. Instr.*, vol. 18, pp. 229 and 267, 1898.
9. Leduc. *Journ. de Phys.*, vol. 1, p. 561, 1902.
10. Patterson and Guthe, *Phys. Rev.*, vol. 7, p. 257, 1898.
11. Richards, Collins and Heimrod, *Proc.* Am. Acad., vol. 35, p. 123, 1899. Richards and Heimrod, *Proc.* Am. Acad., vol. 37, p. 415, 1902.
12. Rodger and Watson, *Phil. Trans.*, vol. 186, p. 631, 1895.
13. Behn, *Wied. Ann.*, vol. 51, p. 105, 1894.

normal ion. Besides, this substance, formed at the anode, must be a reducing agent, since oxygen tends to eliminate it. The exact chemical constitution of the substance is not known.

The main problem is to prevent the anode solution from reaching the kathode. For this purpose Richards places the silver rod, which forms the anode, in a fine grained porous cup and removes from time to time the solution collecting at the bottom.

Guthe[14] fully corroborated Richards' results, but proposed a different form of the anode. The bottom of a wide porous cup is filled with granulated silver and upon this a large silver plate is pressed. In this type the rather inconvenient frequent removal of the solution was found to be unnecessary. The heavy solution is prevented by the porous cup from rapid diffusion and breaks up to a large extent when it remains in contact with silver. This secondary reaction, he believes, gives rise to the formation of the well-known dark anode slime, which is pure silver when the anode is pure.

Other arrangements may be adopted to prevent the anode solution from reaching the kathode. The latter may for instance be suspended above the anode, or the two electrodes be placed in different vessels, connected by a siphon. From a practical point of view the latter types are however less convenient than the two described above.

4. Another source of trouble may arise from the contact of the solution with filter paper. The organic substances contained in the latter may act chemically upon neutral silver nitrate solution.[15] Filter paper should, therefore, not be used in the preparation of the electrolyte nor in the voltameter.

5. As Guthe pointed out, we can distinguish two distinct types of silver voltameters, according whether the heavy anode solution reaches the kathode or not. The former to which the ordinary type and those proposed by Patterson and Guthe and by Leduc belong will on the average yield a deposit one part in 2000 larger than the second, *i. e.*, Richards' and Guthe's types. Of course, for practical purposes, we must select the type which will give the most concordant results. As the investigations referred to show, we can rely upon the porous cup voltameter to within one part in 20,000, even for independent series of experiments; it would, there-

14. Guthe, *Phys. Rev.*, vol. 19, p. 138, 1904.
15. Reichsanstalt, *Zeit. f. Instr.*, vol. 22, p. 156, 1902.

fore, be a decided step in advance, if one of these types were substituted for the one now in common use. This would necessitate a change in the accepted value of the electro-chemical equivalent of silver, as will be shown later on.

6. Whether or not there are other disturbing factors of minor importance, only an extended research with the porous cup voltameter will show. Some of the earlier experiments are not conclusive in this respect; they were made with the usual type, and often the differences observed amount to less than what we may expect in this form of voltameter. Besides, different investigators frequently flatly contradict each other.

In the silver voltameter a neutral solution of silver nitrate is recommended. To test the neutrality it seems best to precipitate the silver by means of neutral sodium chloride solution and test the filtrate with methylorange. If the crystals contain acid it may be well to melt them in a platinum crucible.

As Kahle has shown, the solution becomes acid in being used. It is apparent that if an ion is formed containing more silver than corresponds to the normal salt, there will be some free acid left. Under such conditions the deposit will be too heavy and the acid is frequently held responsible for it. But it is different, if before electroysis free acid has been added to an originally neutral solution. In this case Leduc found the deposits one part in 5000 lighter than without the addition of acid. In fact, if the original amount of free acid surpasses a definite percentage, then on electrolysis the amount decreases. There exists a chemical equilibrium between the complex ions and those of the acid. I believe that the addition of acid to the anode side of a porous cup voltameter will be of help in either preventing the formation of the complex ion or in breaking it up.

The Reichsanstalt recommends not to use acid lest impurities of the anode pass into solution. The influence of impurities in the solution seems, however, to be of little importance, as shown by Rayleigh and Mrs. Sidgwick, who added a large proportion of copper-sulphate to the solution, and by Leduc who added copper-sulphate and also potassium nitrate. The deposits did not contain any of these impurities. It may be stated as a general rule that metals which require a higher kathodic difference of potential than silver will not be found in the deposits, if the current is not too large.

The presence of rarer metals would seem to be more serious, but they are hardly ever found in appreciable quantities in commercial silver, and, moreover, their electro-chemical equivalents are not very different from that of silver. Extreme care in the selection of material for the electrolyte as well as the anode seems, therefore, to be unnecessary. We may even use a soluble electrode of a metal, like zinc, and still obtain satisfactory results, as Richards and Heimrod proved.

7. One great objection is found in the tendency to looseness which the silver obtained from nitrate solution frequently shows. The addition of a small proportion of silver acetate improves greatly the texture of the deposit, but as was shown by Rayleigh and Mrs. Sidgwick, the deposit is always too heavy, possibly due to an inclusion of liquid. The same observers employed silver chlorate as electrolyte and obtained results closely agreeing with those given by a silver nitrate voltameter. Deposits from cyanide solution are pure white and show no tendency to looseness. Leduc[16] has made some experiments with potassium silver cyanide, but the amount of silver collected was entirely too small, which he attributed to a simultaneous development of hydrogen and silver at the kathode and to an occlusion of the former in the silver. Farup,[17] however, has shown that hydrogen is not produced, but that the silver is dissolved by potassium cyanide if air is present in the solution. He employs, therefore, a silver voltameter with potassium silver cyanide as electrolyte, but saturates the solution with hydrogen.

The results obtained by him are quite satisfactory, though I believe that with larger deposits trouble may arise due to occlusion of the liquid in the deposits. For small currents, however, this form seems to be very useful. It is claimed that even deposits from silver nitrate solution keep some of the liquid included. This will show itself in a decrease of weight when the deposit is heated to nearly red heat, the nitrate being decomposed. According to Rayleigh and Mrs. Sidgwick, there was sometimes no loss on heating, but perhaps more often a slight decrease. Kahle advises a treatment for 10 to 20 minutes with water at a temperature of 70 deg. to 90 deg. C., to insure the complete removal of the mother liquid. Richards also found a slight amount included; but Gray

16. Leduc, *Rapports* Congr. Internat. de Phys. 1900, vol. 2, p. 440.
17. Farup, *Zeit. f. Electroch.*, vol. 8, p. 569, 1902.

claims that with proper washing the plates may be heated without any sensible loss of weight.

8. The question of the solubility of silver in different liquids is one of great importance. According to Richards and Heimrod pure silver when boiled with a silver nitrate solution will produce nitrite of silver in small quantities, but the Reichsanstalt makes the statement that this is not the case and that, therefore, under normal conditions a reduction to nitrite cannot be observed in a silver voltameter. Kahle, Myers and Merrill[18] observed a decrease of the weight of silver, when it was treated with warm water, but Richards, Collins and Heimrod, Leduc and Guthe could not detect any change when the deposit was left standing *under* water for hours.

The concentration of the silver nitrate solution seems to affect only the texture of the deposit, which has a tendency to looseness, if the solution is too weak in relation to the current. Though Gray considers it a mistake to use solutions containing more or even as much as 10 per cent of silver nitrate, all other observers deny any influence of concentration and generally recommend high concentrations, i. e., from 15 per cent to 30 per cent.

The Reichsanstalt has found that silver oxide is almost insoluble in concentrated nitrate solution, but the experiments referred to above show that solutions treated with the oxide are favorable to the formation of the complex ion and will yield too much silver.

9. Schuster and Crossley stated that the deposits of silver in vacuo were about one part in 1000 larger than those obtained from solutions surrounded by air, and these again larger than those formed in an atmosphere of oxygen. The former result was verified by Kahle, Richards and Myers.[19] The latter also found an increase when the liquid was saturated with nitrogen, but a decrease when the dissolved gas was carbon dioxide. It is reasonable to suppose that the increased weight of the deposit is due to the removal of oxygen from the solution and not to a change in pressure. In addition Merrill showed that an increase of pressure to 103 atmospheres has no appreciable effect.

Rayleigh and Mrs. Sidgwick observed an increase of deposit with increase of temperature, Leduc a decrease, Richards, Collins

18. Merrill, *Phys. Rev.*, vol. 10, p. 67, 1900.
19. Myers, *Wied. Ann.*, vol. 55, p. 288, 1895.

and Heimrod obtained as well at 60 deg. C. as at 0 deg. C. a larger deposit than at 20 deg. C.

10. Almost all observers agree that the size of the kathode makes no difference. According to Schuster and Crossley too great a current density at the anode is accompanied by a smaller deposit; according to Leduc just the opposite is the case, while Merrill could find no measurable effect due to a variation in the size of the electrodes. Guthe's experiments lead to the conclusion that in the porous cup voltameters the size of the anode does not come into account. With the usual type of voltameter Kahle obtained a somewhat larger deposit on a silver kathode than on platinum and considers, therefore, as normal deposits such obtained on silver. Richards and Heimrod confirm this observation but find that with a porous cup voltameter no such difference appears. Guthe also obtained identical results as well when the kathode was platinum as when silver had been previously deposited on it. The explanation for Kahle's results is to be sought in the action of silver upon the heavy anode liquid, mentioned above.

The Electrochemical Equivalent of Silver.

11. The electro-chemical equivalent of silver has been determined repeatedly by absolute measurements, i. e., by means of instruments which allow a calculation of the current in terms of the fundamental units of mass, length and time. Among the earlier investigations only those of Rayleigh and Mrs. Sidgwick, and of Fr. and W. Kohlrausch can be considered accurate. In order to express all measurements in terms of the same standard, the different values found have been reduced to those given by the porous cup voltameter, and these are given in the last column of the following table. The corrections used are those found by Richards and Guthe for the various types. Since in most cases the exact conditions of the experiments are unknown, these corrected values will simply give a general idea of the agreement between different observers; therefore, it was thought unnecessary to take into account the possible effect of included mother liquid.

TABLE I.

Observer.	Year.	Voltameter.	Method.	Electro-chemical equivalent.	
				Found.	Corrected.
Mascart[1])	1884	Usual type.....	Current balance.....	1.1156 mg.	1.1150 mg.
Fr. and W. Kohlrausch.....	1884	"	Tangent galv.....	1.1183	1.1177
Rayleigh and Sidgwick.....	1884	"	Current balance.....	1.1179	1.1175
Gray.....	1886	Plate voltameter..	Sine galvan.....	1.1183	1.1177
Koepsel[2]).....	1887	Usual type.....	Current balance.....	1.1174	1.1168
Pellat and Potier[3])	1890	"	"	1.1192	1.1186
Patterson and Guthe.	1898	Silveroxide type..	Electrodynamometer.	1.1192	1.1182
Pellat and Leduc[4]).....	1903	Leduc's type.....	Current balance.....	1.1195	1.1188
van Dijk and Kunst[5]).....	1904	Usual type.....	Tangent galv	1.1182	1.1176

1) Mascart, *Journ. de Phys.*, vol. 2, p. 109, 1882 and vol. 3, p. 283, 1884.
2) Koepsel, *Wied. Ann.*, vol. 31, p. 250, 1887.
3) Pellat and Potier, *Journ. de Phys.*, vol. 9, p. 381, 1890.
4) Pellat and Leduc, *C. R.*, vol. 136, p. 1649, 1903.
5) van Dijk and Kunst, *Ann. d. Phys.*, vol. 14, p. 596, 1904, *Proc.* Kon. Ak. van Wet., vol. 12, p. 441, 1904.

From this list we see that the results obtained so far are not very satisfactory. Redeterminations in absolute measure by using a reliable form of voltameter are highly desirable.

12. The electro-chemical equivalent of silver may also be expressed in terms of the electromotive force of a standard cell, i. e., by comparing the electromotive force of the cell with the potential difference produced by the current at the terminals of a known resistance. The electro-chemical equivalent will depend upon the value chosen for the electromotive force of the standard cell. The legalized value for the Clark cell is 1.434 volts. But this is probably too high. In Germany the electromotive force of the Clark cell is derived from silver voltametric measurements, and the Reichsanstalt has chosen as the working value 1.4328 volts at 15 deg. C. In the following table the electro-chemical equivalent of silver is calculated as well for an electromotive force = 1.434 as for 1.433 volts.

TABLE II.

Observer.	Year.	Electro-chemical equivalent.			
		$E = 1.434$ volts.		$E = 1.433$ volts.	
		Usual type.	Porous cup V.	Usual type.	Porous cup V.
Carhart[1])	1882	1.1172 mg.	1.1167 mg.	1.1180 mg.	1.1175 mg.
Rayleigh and Sidgwick...	1884	1.1183	1.1178	1.1192	1.1187
von Ettinghausen[2])	1884	1.1180	1.1175	1.1188	1.1183
Glazebrook and Skinner...	1892	1.1183	1.1178	1.1191	1.1186
Perot and Fabry[3]).....	1898	1.1193	1.1188	1.1120	1.1196
Kahle	1898	1.1173	1.1167	1.1180	1.1175
Guthe	1904	1.1174	1.1168	1.1181	1.1176

1) Carhart, *Am. Journ. Sci.*, vol. 28, p. 374, 1884.
2) Von Ettinghausen, *Zeit. f. Electrotechnik*, vol. 2, p. 484, 1884.
3) Perot and Fabry, *Ann.* Fac. des Sci. Marseille, vol. 8, p. 201, 1898.

In the case of Perot and Fabry, who used a Clark cell at 0 deg. C. and found its electromotive force to be 1.4522 volts, using 1.118 mg as the electro-chemical equivalent, the difference of 0.0164 volt given by the Reichsanstalt has been used to reduce to 15 deg. C., instead of the ratio given by them. The latter would give 1.1180 mg in the first column and corresponding values in the others, and make the agreement with the earlier experiments a very close one.

The large differences between the earlier and the more recent comparisons can hardly be due to the silver voltameter alone. Doubtless the Clark cell comes in for its share.

Wolff and Carhart and Hulett have lately discovered an electrolytic method of preparing mercurous sulphate. Cadmium standard cells, in which this substance is used, show according to preliminary reports an excellent agreement among themselves, and no variation in their electromotive force in course of time,— as far as can be ascertained during a relatively short period.

With the improvement of our standard of electromotive force and the construction of a reliable silver voltameter, a wide and interesting field for research has been opened.

Discussion.

Dr. K. E. Guthe: I can not close this paper without emphasizing one point with reference to the alleged superiority of the standard cell over the silver voltameter in the measurement of an electrical current. I still believe that the voltameter gives as accurate results as the standard cell. It must be admitted, that for laboratory use, it is easier to measure a

current by fall of potential over a resistance. And while I believe the standard cell will win out in the end, nevertheless, I am sure the silver voltameter will always be a valuable instrument for checking our work with the standard cell.

Dr. R. T. GLAZEBROOK: I have already spoken a great deal at this meeting on these subjects, and do not wish to detain you very long. I am glad to have this opportunity of expressing my appreciation of the paper just read. The labor involved in producing such a paper is extreme, and its value can hardly be overestimated. I wish to particularly emphasize one point that Doctor Guthe has brought out and with which I entirely agree, and that is this, that the experiments of Mr. Skinner and myself must be held to relate solely and simply to the form of silver voltameter used by us in that experiment.

Lord Rayleigh also, I think, would disclaim the view that he had determined the electrochemistry of silver, or that he had investigated completely all the conditions that ought to be satisfied before you can say that the result arrived at was the electrochemical equivalent of silver.

In the specification for the use of the voltameter which was published by the English Board of Trade, full details are given as to the silver voltameter which he used, and which has often been used in England. It is, I think, interesting to point out our experiments as giving the ratio between the electrochemical equivalent of silver and the e.m.f. of Clark's cell. It may be the value for the electrochemical equivalent of silver derived from the experiments with the electrodynamometer needs correction, and if so that will account for the higher value of the e.m.f. of the cell, which we have always obtained in England. This is a point which I hope will be settled before very long, because, as I have already explained, an ampere balance from which we anticipate very excellent results is now under construction in England.

I will close by expressing my thanks to Doctor Guthe, and I believe that every one interested in this subject will find his work of very great importance.

Dr. W. D. BANCROFT: I should like to ask whether experiments have been made with a rotating cathode inside the porous cup. In that case there would be practically no differences of concentration in the cathode solution. You would get a better deposit, and, if necessary, you could run a higher current-density and precipitate more silver.

Dr. K. E. GUTHE: Doubtless the rotating cathode gives very satisfactory results for electrochemical analysis and it would probably be of help in silver voltametric work. The trouble with the voltameter originates, however, at the anode. One objection to a rotating electrode is the more complicated arrangement of apparatus necessitated by it.

Dr. W. D. BANCROFT: The other point is apparently settled, that in the case of silver there is no difference in the weight when deposited on a platinum or a silver cathode, but that is not the case with other metals standing higher in the voltaic series. In some experiments we made on the plating of zinc, we found that in sulphate solutions there is great difficulty in getting a good deposit of zinc on a copper cathode while a zinc cathode gives satisfactory results.

Mr. S. S. SADTLER: I would like to ask Doctor Guthe whether silver nitrate would not be a good silver salt to use as electrolyte. He speaks of action on the electrodes at the surface of the electrolyte, which might be avoided by the silver salt being in a lower state of oxidation.

Dr. K. E. GUTHE: In my article a number of silver salts besides the nitrate have been mentioned, but they do not seem to have proved superior to the nitrate. I am not aware that the nitrite has ever been used in a voltameter.

Doctor Bancroft then took the chair, and Doctor H. S. Carhart said:

I have only a few remarks to make on Doctor Guthe's admirable paper. In the first place, I should like to explain that the determinations I made of the e.m.f. of Clark cells at that time were incidental to some other work I was doing. I made only two determinations of e.m.f. and they could not be reduced until three years after the experiments, for the reason that the electrochemical equivalent of silver was not known with sufficient accuracy. They were not reduced until after the publication of Lord Rayleigh's paper in 1884, I think it was. This work was done in the winter of 1881 or spring of 1882, and the only Clark cell I think I had ever seen at that time was the one I used. It was a large one which was in the laboratory at Berlin. It was hermetically sealed, and in it was sealed a thermometer. The instrument itself was provided for me by Professor Helmholtz at the time. So, if I reached a fairly good value as determined by later research, it was perhaps more good fortune than the result of any very careful work.

Now, further, I must confess that I am somewhat surprised to see the wide variations and difficulties, brought out in this paper of Doctor Guthe, which occur in the use of the silver voltameter. We have been told by Professor Kohlrausch that the chemical reactions or relations in the silver voltameter are much simpler than they are in the standard cell; but after reading this paper, I think that statement is very doubtful. It strikes me there are many more points left unsettled in the use of the silver voltameter than there are in the standard cell. At all events, the discrepancies now are at least as great as we find in standard cells, and I believe that the discrepancies with the silver voltameter are greater than those in standard cells. But it must be admitted by everybody that when we are going to measure currents we can not use the silver voltameter, but must use standard resistances and a standard cell with a potentiometer.

I wish to add one more remark with reference to the difference in the e.m.f. of the Clark cell obtained by the silver voltameter at the Reichsanstalt and elsewhere. It is not generally known that the value obtained by means of the silver voltameter at the Reichsanstalt was corrected by reference to the ratio between the e.m.f. of the Clark cell and that of the cadmium cell measured by a direct comparison, and this fact accounts for a part of the difference. The procedure was as follows: The e.m.f. of the Clark cell at 15 deg. was determined by the silver voltameter, or at least the results were corrected to 15 deg. The e.m.f. of the cadmium cell at 20 deg. was also measured by the silver voltameter; and thus the ratio between the Clark cell at 15 deg. and the cadmium cell at 20 deg.

was obtained. This ratio has also been determined by direct comparisons, and several series of such comparisons have been carried out. The inference then was that the directly measured ratio of Clark 15 deg. to the cadmium 20 deg. was more reliable than that obtained by the use of the silver voltameter. The ratio obtained by the silver voltameter was then corrected. The value of the e.m.f. of the Clark was reduced, and that of the cadmium cell raised, in order to make the ratio correspond to that obtained by direct measurement. The reduction in the cadmium cell and the increase in the Clark was of course small. That correction accounts for a part of the difference in results.

The following paper was then read by Professor Carhart.

A STUDY OF THE MATERIALS USED IN STANDARD CELLS AND THEIR PREPARATION.*

BY PROF. H. S. CARHART AND PROF. GEO. A. HULETT.

PART I.

MERCUROUS SULPHATE AND STANDARD CELLS.

BY GEO. A. HULETT, *Assistant Professor, University of Michigan.*

Variations in the e.m.f. of standard cells have been traced to the Hg_2SO_4 used as depolarizer, and especially Jaeger and St. Lindeck, Zeitsch. f. Instk. 21, 33, 1901, have shown that cells made with mercurous sulphate from different sources may differ as much as 0.0002 *V*. It is also well known that standard cells, when first set up, have a high e.m.f., but in a month or so settle down to a constant value. Also little is known of changes taking place when Hg_2SO_4 is exposed to the light.

In conjunction with the work of Professors Carhart and Patterson on the absolute determination of the e.m.f. of the cadmium cell, the chemical side of the cell has been taken up and the following results obtained.

The preliminary work was the testing of various samples of Hg_2SO_4 from the point of view of their use as a depolarizer. In each leg of an *H* cell was placed mercury and the cell was then filled to above the cross-bar with dilute H_2SO_4; with mercurous sulphate on the mercury there was no e.m.f. provided the Hg_2SO_4 in each leg was from the same sample, but different samples generally gave an e.m.f. One preparation (electrolytic, to be described later) was taken as a standard and all others compared to this reference Hg_2SO_4.

Preparations of well-known makes differed markedly often by 0.001 *V* when tested in this way, and my own preparations made in various ways showed little agreement. That prepared by *adding* a solution of $HgNO_3$ slowly *to* H_2SO_4 (1 to 6 vol.) with rapid

* This investigation, carried out with the aid of a grant from the Elizabeth Thompson Science Fund, is still in progress. The authors desire to express their indebtedness to the trustees of this fund.

stirring seemed best, that is, it was practically the same as the electrolytic, while the sample made by adding $HgNO_3$ to $CdSO_4$ solution showed +.0002 *V*. These results led me to devise the following electrolytic method of preparing pure Hg_2SO_4. It seemed desirable to use only Hg and H_2SO_4, but these substances interact with sufficient rapidity only when concentrated H_2SO_4 is used and at a high temperature; also this product carries H_2SO_4 which is difficult to remove, and gives a high e. m. f. in a single potential electrode, as shown by Sauer, *Zeitsch. Ph. Ch.* 47, 182, 1904.

The desire to use dilute H_2SO_4 at a low temperature suggested the idea of using an electric current and making the mercury the anode with a Pt. kathode in the dilute H_2SO_4. Ostwald, *Zeitsch.*

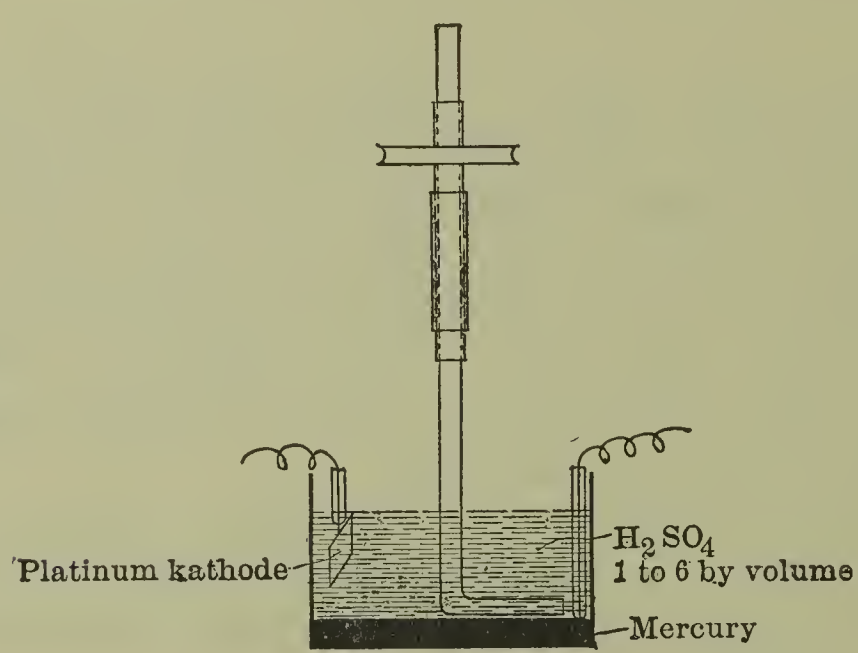


FIG. 1.

Ph. Ch. 15, 500 (1895), and Nernst, *Zeitsch. Ph. Ch.* 34, 129, have shown that Hg under such conditions goes into solution as mercurous mercury, and in our case H_2 is separated on the Pt. kathode; later when the electrolyte contains mercurous ions some of these are also deposited on the Pt. but due to the slight solubility of Hg_2SO_4 (0.400 *gm/L.*) and the large excess of *H* ions, relatively little mercury is deposited on the kathode.

As soon as the electrolyte becomes saturated with Hg_2SO_4 the salt begins to separate in a crystalline form and collect on the mercury. A motor-driven stirrer is needed to keep the surface of the mercury free of Hg_2SO_4 and in contact with the electrolyte. Fig. 1 gives a sectional view of the apparatus needed to prepare the electrolytic mercurous sulphate.

In the bottom of a strong beaker glass or dish is placed mercury

1 to 2 cm deep and on this is sulphuric acid (1 to 6 by volume) some 10 cm deep. A Pt. electrode of convenient size is suspended in the acid, while contact is made with the mercury in the usual way with a Pt. wire, protected, except at its point, with a glass tube. One may use a current density of 0.3 amp. to 100 cm^2 mercury surface or even more when all is working nicely. The stirring is important, the *L* part of the stirrer should pass close to the surface of the mercury and quite rapidly, but not so rapidly that the surface of the mercury will be broken into globules. The stirrer is best provided with metal bearings that do not abrade. If not sure of the purity of the mercury it is best to remove it after running a few hours and start afresh. The mercury is easily and neatly removed by a separatory funnel.

One hundred cm^2 mercury surface should yield about 3 gm per hour, and it is well to prepare the Hg_2SO_4 in a dark room or out of bright light, as light decomposes the sulphate. If too strong acid is used or the stirring is too rapid the product will be quite grey, due to finely divided mercury, but with continued and steady agitation with mercury and acid the Hg_2SO_4 becomes white, crystalline and fairly large grained.

The sulphate should be preserved in contact with mercury and under acid (1 to 6 vol.) in the dark until needed. Analysis has been made of this product showing it to be Hg_2SO_4, while its behavior in the standard cells shows that it is a very pure product, and it will be seen later that it does not contain a trace of $HgSO_4$ (ic) although there is a little mercuric mercury in the solution from which it is separated.

Cells made up with this electrolytic Hg_2SO_4 as depolarizer,—provided precautions are taken to avoid hydrolysis — show a much better agreement than has hitherto been obtained in standard cell work. This is shown by the measurements on cells (D_1 to D_4) and (F_1 to F_{10}) by Professor Carhart, as given in this paper, the e.m.f. at 21.1 deg. being 1.01908 int. volts for the cadmium element, a value that is 0.00030 *V* lower than cells constructed according to the old method.

We have based our method of constructing the cells on the facts brought out in the following study of the equilibrium in the positive leg of the cadmium cell and of the hydrolysis of mercurous sulphate.

Abel, *Zeitsch. Anorg, Chem.* 26, 361 (1901), has shown that whenever we have mercury in contact with a solution containing

a mercury salt there will result an equilibrium between the (ous) and the (ic) mercury in solution and the metal. For the nitrate Abel found the ratio of $\frac{Hg\ (ous)}{Hg\ (ic)} = 200$. There is relatively little (ic) mercury in a solution that is in equilibrium with mercury; and since the mercuric sulphate is more soluble than the mercurous, if we bring the system Hg-Salt-solution to equilibrium, the salt cannot contain mercuric sulphate, but would be only mercurous sulphate. To test this point some mercuric sulphate was recrystallized from dilute H_2SO_4. The mass soon became grey, due to finely divided mercury, but on continued agitation, the salt became white and beautifully crystalline. A cell was made up from this salt and showed at 21.1 deg. 1.01911 volts, a value practically identical with the electrolytic Hg_2SO_4, a result that substantiates the conclusions drawn from Luther and Abel's work.

In the positive leg of the cadmium cell we have Hg, Hg_2SO_4 and $CdSO_4\ \frac{8}{3}H_2O$ in contact with a saturated solution and we are then to conclude that here also the solution will contain both mercurous and mercuric mercury, while the solid salt is only Hg_2SO_4 and possibly a basic salt.

A solution that was brought to equilibrium with Hg, Hg_2SO_4 and $CdSO_4\ \frac{8}{3}H_2O$ at 25 deg. was carefully analysed by adding a little KCl which precipitated the mercurous mercury as HgCl. It was found that a liter of such a solution contained 1.090 gm of mercurous mercury, a surprisingly large amount in view of the solubility of Hg_2SO_4 in dilute sulphuric acid, 0.400 gm/L.

It has been further shown by Abel l. c. that in the absence of the metal we may remove the mercurous mercury and not disturb the mercuric mercury; so the filtrate from the above determination contained all the mercuric mercury originally present; and if now we bring this filtrate again in contact with metallic mercury the old equilibrium ratio will be established; and, since a slight excess of KCl is present, the (ous) mercury will separate as fast as formed. Thus mercuric mercury may be detected and determined.

It was found that on bringing the above-mentioned filtrate into contact with mercury HgCl began to form at once and collect as a coat on the mercury. The amount is small and difficult to determine quantitatively. One result indicated the ratio of $\frac{Hg\ (ous)}{Hg\ (ic)}$ = about 80 for the cadmium sulphate solution.

Theoretically, it should make no difference whether we construct a cell with mercurous or mercuric sulphate; the final equilibrium would be the same in either case; but the conditions in a cell are very unfavorable to attaining equilibrium; and, mercuric sulphate being more soluble, would increase the total e.m.f. of the cell.

The Hydrolysis of Mercurous Sulphate.

Mercurous salts on dissolving yield some mercuric mercury and metal and tend to come to an equilibrium as indicated above; therefore it was deemed advisable always to keep an excess of mercury present when working with mercurous sulphate. Accordingly some 15 grams Hg_2SO_4 with a large excess of Hg was shaken with 400 c. c. of water at 25 deg. until equilibrium was established. The salt remained white, that is, the yellow salt commonly observed did not appear. The solution contained 0.00235 moles of mercurous mercury per liter and 0.00225 moles SO_4 and showed a conductivity of 0.000975 ohm^{-1} cm^{-1} at 25 deg. The solution was syphoned from the solid and 400 c. c. more water added and again shaken and this process repeated, waiting each time until equilibrium was obtained. The conductivity of the successive portions remained the same 0.000975; also analysis showed the composition of these successive solutions to be constant. The residue did not turn yellow, but did in time take on a greyish tinge. Evidently the commonly-observed yellow salt has little to do with the hydrolysis of mercurous sulphate. The 22d solution was like the preceding, but the 23d showed a marked drop in the conductivity, while the succeeding portions now had a conductivity of only 0.000060, and analysis showed a correspondingly small amount of mercury present, only 0.037 mg mercurous mercury in a liter.

Evidently the mercurous sulphate had completely disappeared and the residue (8.5 grams) was the completely hydrolysed product. It was greyish white and crystalline. Analysis showed 84.30 per cent of mercury and 10.50 per cent of SO_4. These percentages do not show a close agreement with the formula given by Gouy (Cr. 130, 1399, 1900) $(HgOH)_2\ Hg_2SO_4$, which requires 86.02 per cent Hg and 10.32 per cent SO_4. However, it was found that the basic salt does not dissolve as such, but is decomposed by the continued action of water[1], and the above salt had been in contact with much water after forming. The results, therefore, confirm

1. Compare Cox, "Ueber basische Quecksilbersalze," *Zeit. Anorg. Ch* 40, 146, 1904.

Gouy's formula; and further, since the solution contained uniformly 0.00235 eq. ous mercury to 0.0022 of SO_4, there must be $HgHSO_4$ in solution, the slight excess of mercury over SO_4, coming from the slight solubility of the basic salt. We are to conclude then that a solution of 0.0023 moles of $HgHSO_4/L$ will not hydrolyse mercurous sulphate, and might safely be used in a preliminary washing of the sulphate.

From the above, then, the hydrolysis of Hg_2SO_4 takes place as follows:

$$3Hg_2SO_4 + 2H_2O = (HgOH)_2Hg_2SO_4 + 2HgHSO_4.$$

And further, a liter of water hydrolyses 1.75 gm Hg_2SO_4 leaving 0.90 gm of $(Hg_2OH)_2\ Hg_2SO_4$ as a residue while 0.68 gm $HgHSO_4$ go into solution.

It seemed further advisable to know the concentration of sulphuric acid which would prevent the hydrolysis of Hg_2SO_4 and this information was sought by following the solubility at 25 deg. of Hg_2SO_4 in H_2SO_4 of varying concentrations. Here again mercury was always present in excess and care was taken that the system Hg, Hg_2SO_4 solution was really in equilibrium before analysis was made of the liquid phase. The following table gives the results obtained, the mercurous mercury in 200 c. c. was in each case weighed as HgCl, and in all cases the filtrate showed a brown coloration with H_2S. Here again we find the equilibrium between Hg and (ous) and (ic) mercury in solution. The ratio in these cases was $\frac{Hg\ (ous)}{Hg\ (ic)} = 200.$

Dilution of H_2SO_4	Grms. of HgCl /200 c. c.	Moles of Hg(ous) /L.	Grms. of Hg(ous) /L.
250 L.	.0886	.001880	.376
100	.0755	.001603	.321
50	.0719	.001527	.305
20	.0726	.001537	.307
10	.0768	.001625	.325
5	.0827	.001762	.352
4	.0860	.001826	.365
3	.0925	.001962	.392
2	.0983	.002081	.416
1	.1034	.002208	.442
$\frac{3}{4}$	.1022	.002121	.424
$\frac{1}{2}$	.0908	.001932	.386
$\frac{1}{4}$	.0411	.000871	.174

The results plotted in the form of a curve with concentrations of mercurous mercury as ordinates and dilution of H_2SO_4 (number of liters which contain a molecular weight) as abscissa show the peculiar behavior of the salt. Starting with the most concentrated acid H_2SO_4 ($V = 1/4L$) (eight times normal) the solubility is very small, 0.174 gm of (ous) mercury in a liter, but the solubility increases rapidly with dilution of the acid and is a maximum at H_2SO_4 $V = 1L$. Here there is a sharp break in the curve, the solubility decreases rapidly with dilution and linear from ($H_2SO_4 V = 1L$) to ($V = 4L$) where another less marked break

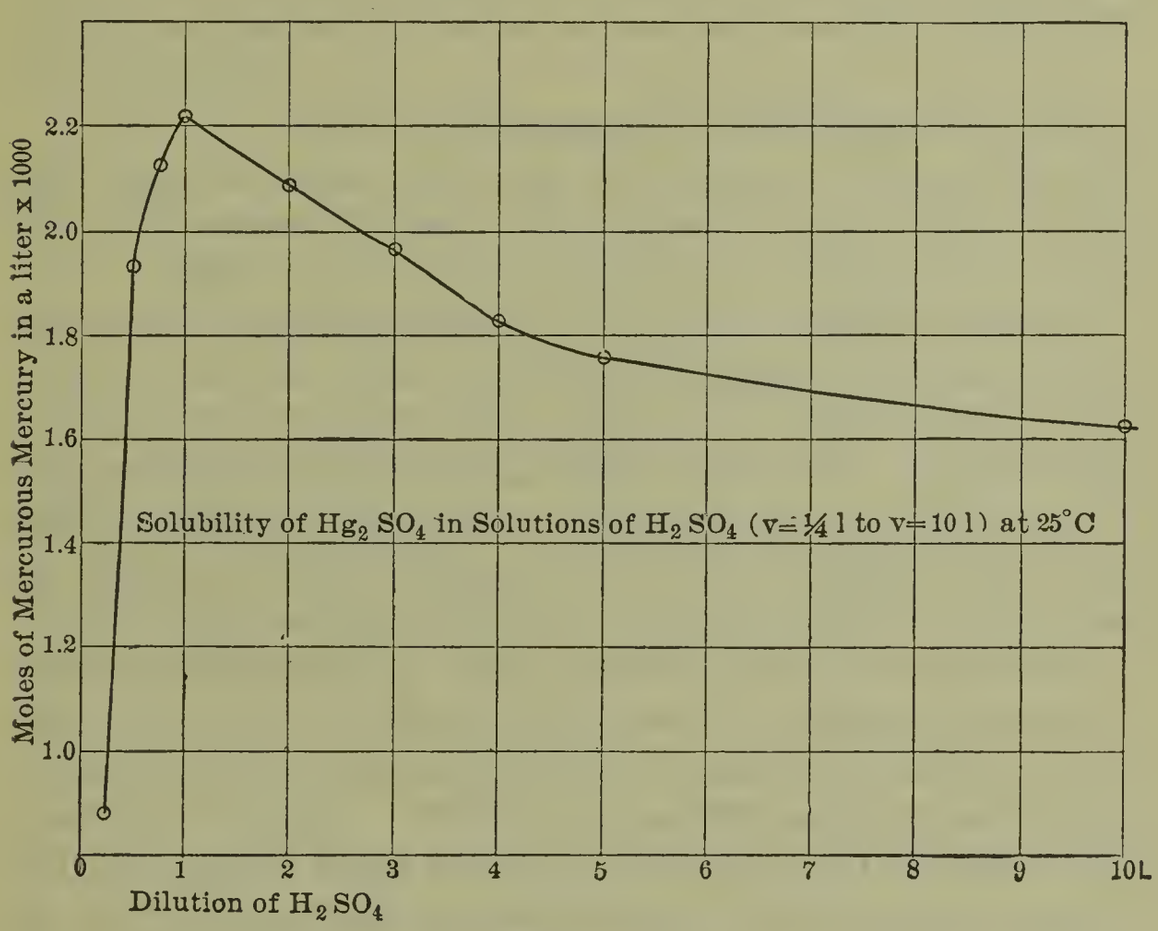


FIG. 2.

occurs. From $V = 4L$ the decrease in concentration of (ous) mercury is less rapid, becomes a minimum at $V = 40L$ and then begins to increase to 0.371 gm of (ous) mercury in a liter at $V = 250L$.

The cause of the interesting break at H_2SO_4 $V = 1L$ has not yet been fully ascertained, but at H_2SO_4 $V = 4L$ hydrolysis has already begun to be effective, yielding $HgHSO_4$ in solution and this acts against the decreasing solubility, and at H_2SO_4 $V = 40L$ actually reverses the direction of the curve.

It was deemed advisable to prepare Hg_2SO_4 electrolytically from H_2SO_4 of greater strength than ($V = 1L$) and a sample was made from H_2SO_4 $V = 1/3L$ and washed with alcohol to remove the acid and water and then analysed. The result was 80.50 per cent Hg and 19.40 per cent of SO_4 (theory requires 80.65 per cent mercury and 19.36 per cent SO_4). A second sample of Hg_2SO_4 was made from acid of a strength falling between $V = 1L$ and $V = 4L$, that is on the straight line beyond the break at H_2SO_4 $V = 1L$. Analysis of this sample showed 80.77 per cent Hg and 19.25 per cent SO_4 indicating the presence of a very small amount of basic salt.

Cadmium cells were now made up with these two samples and the one made from the last sample ($V = 2L$) gave the higher e.m.f. by 0.0001 V, indicating the presence of basic salt.

Hg_2SO_4 should, therefore, be made from acid stronger than H_2SO_4 $V = 1L$ and the strength first chosen by chance 1 to 6 by volume, about H_2SO_4 $V = 1/3L$, seems to be about right.

A cadmium cell was now made up in the usual way only the depolarizer was the completely hydrolysed salt and the e.m.f. is only 1.01620 V after two months and it has not yet reached its constant value. This result agrees with the slight solubility found for the hydrolysed salt assuming it is also less soluble in $CdSO_4$ solution than Hg_2SO_4. It is to be noticed that the greater the concentration of mercury in the solution of positive leg of the cell the greater the total e.m.f. and *vice versa,* for solutions of mercury are decidedly negative to the metal mercury; e. g., in the single potential calomel electrode the solution contains 0.030 gm Hg/L only, but the potential difference is 0.560 V. Above we have found that a saturated Cd_2SO_4 solution dissolves about 1.1 gm to a liter of (ous) mercury and it seemed probable that the e.m.f. in the positive leg would be quite large. This was tested by a calomel electrode which was joined to a cadmium cell and it was found that the potential difference between the cadmium amalgam and $CdSO_4$ solution was only 0.0862 V, while in the positive leg the potential difference was 0.934 V, a surprising result, but in accord with the solubility of Hg_2SO_4 in a saturated $CdSO_4$ solution. In the determination of the single potential differences no account was taken of the potential difference at the junction of the KCl/n solution of the calomel electrode and the $CdSO_4$ solution of the cell, as the necessary data for calculation is not at hand; but it is known that such potential differences are small.

The above results emphasize the importance of the role played by the depolarizer Hg_2SO_4 on the e. m. f. of standard cells. Further indirect evidence on this point was obtained by the following cadmium cells I_9 and I_{10} set up in the usual way except in I_9 the solution used to fill the cell contained some $ZnSO_4$ (1 part $ZnSO_4$ to 99 parts $CdSO_4$) and in cell I_{10} the amalgam contained zinc (1 part to 99 Cd). I_9 has the same value as another cell made with same materials, but without $ZnSO_4$, indicating that $ZnSO_4$ — the most probable impurity to be expected in the $CdSO_4$ — is not to be feared. The cell I_{10} showed an e. m. f. 0.00013 *V* higher than I_9, that is, the 1 per cent Zn affected the e.m.f. by .00013 *V* only; and in time I_{10} will no doubt agree with I_9 since Zn will go into solution and deposit Cd.

A cell was now set up with electrolytic Hg_2SO_4 washed to avoid hydrolysis, but then mixed with about one-sixth its weight of the completely hydrolysed salt. The cell had the value 1.01939 *V* 21.1 deg. at first and is now, after a month, 1,01934. This indicates that a mixture of Hg_2SO_4 and $(Hg_2OH)_2\ Hg_2SO_4$ gives a higher e.m.f. than either alone, that is, yields a greater concentration of mercury in the solution in the positive leg of the cell. If precautions are taken to prevent hydrolysis we have only Hg_2SO_4 present, and the cadmium cell has the value 1.01908 int. volts at 21.1 deg.

With proper precautions in the preparation and washing of the Hg_2SO_4 the cadmium cells seem to be reproducible to at least five parts in 100,000 and it seems probable that more experience will even reduce this variation. The important point is the rigid exclusion of the hydrolysed product either in the preparation or washing of the Hg_2SO_4. The directions given in the second part embody the results of our work and experiences to date, and it might be added that the washing with absolute alcohol and ether to remove the acid has many points in its favor; but for some reason the cells so constructed are at first some 0.00010 *V* high and only attain the normal value in a month or so, but do not finally differ from those made by washing with $CdSO_4$ solution. The Hg_2SO_4 prepared as directed is distinctly crystalline and the grains of sufficient size to avoid any effect of size of particles on the solubility. The details of the analyses and experimental work given in this paper appeared in full in the *Zeitsch. f. Ph. Ch.* 49, 483 (1904).

PART II.

PREPARATION OF MATERIALS AND CONSTRUCTION OF CELLS.

BY PROF. HENRY S. CARHART, *University of Michigan.*

The chemical research done on mercurous sulphate by Dr. Hulett points out the best method, according to present information, for preparing this salt for use in Clark and Weston standard cells. The present part of this paper will be restricted to directions for preparing the materials entering into standard cells, particularly the Weston Normal Cell, with excess of cadmium sulphate crystals, to the method of setting up cells, and to the results of observations extending over a period of more than a year.

Mercury.

The mercury for the positive electrode and for making the mercurous sulphate should first be thoroughly shaken with a dilute nitric acid solution of mercurous nitrate;[1] and, after drying, it should be distilled in a vacuum at least twice.

Cadmium Sulphate.

Chemically pure commerical $CdSO_4$ $8/3H_2O$ is dissolved at room temperature in its own weight of distilled water, preferably with the aid of a motor-driven stirrer. The solution must be filtered till it is perfectly clear; it may then be placed in a large crystallizing dish in a small room free from dust. It is advantageous to remove the water vapor by appropriate drying agents. The slow crystallization taking place should insure perfectly transparent crystals.

After about two-thirds of the water has evaporated the mother liquor should be poured off and *only the clear crystals should be selected.* Those that are white may be redissolved and added to the mother liquor. The solution is again filtered clear and is left to crystallize as before. The selected clear crystals are rinsed with

1. *Zeit. Ph. Ch.*, 33, 611.

distilled water, drained, and left to dry; or they may be dried by spreading them out on sheets of filter paper.

In crystallizing about five kilogrammes of $CdSO_4$ 8/3 H_2O the final 100 c. c. of mother liquor contained only the merest trace of zinc; and zinc is the chief impurity to be eliminated. It should remain in the mother liquor, since zinc sulphate and cadmium sulphate are not isomorphous.

Moreover, a trace of zinc sulphate mixed with cadmium sulphate produces only an insignificant effect on the e.m.f. of the cell. Cell 19 was made up with a solution containing 1 per cent zinc sulphate and 99 per cent cadmium sulphate. Its e.m.f. is not higher than that of other cells made at the same time and not containing zinc sulphate.

Cadmium sulphate crystals dissolve very slowly. The solubility is increased by heat, but the temperature must not be raised above 40 deg., in order to avoid the formation of a different hydrate. The crystals should be covered with two-thirds their weight of distilled water in an Erlenmeyer flask. A suitable stirrer should keep the water moving over the crystals for at least half a day, preferably in a bath at 25 deg. controlled by a thermostat. The solution should be clear and should remain so. It should be left standing over the crystals, and when it is used it should be saturated at a temperature as high as 25 deg. The saturation of the solution is of great importance in order that the cells may quickly reach electrical equibibrium.

Cadmium Amalgam.

The cadmium amalgam invariably used in all the cells under observation contained 12.5 per cent metallic cadmium. To prepare it the following method is recommended: A large crystallizing dish is nearly filled with a saturated solution of cadmium sulphate slightly acidulated with sulphuric acid. In a small, low crystallizing dish is placed a weighed quantity of pure mercury, and the dish with its mercury is immersed in the acidulated cadmium sulphate solution. The pure cadmium of commerce is melted down into a large flat button with a stick of cadmium attached for electrical connection; or, several of the cadmium rods, bound together, are placed together in a vertical position with their lower ends in the solution and beneath them a small crystallizing dish. If the cadmium button or disk is used, it should be placed in the second low crystallizing dish, which retains the finely divided

anode powder. The metallic cadmium is then made the anode and the mercury the kathode, connection with the latter being made by means of a platinum wire sealed, except at its end, in a glass tube. The fall of potential from anode to kathode should not exceed 0.3 volt. An ammeter should be used to keep account of the quantity of electricity flowing through the cell, until something more than the requisite weight of cadmium has been deposited on the mercury kathode. The small dish containing the cadmium amalgam is then removed from the bath and warmed till the amalgam melts under the cadmium sulphate solution. When cool it forms a beautiful crystalline disk. The solid amalgam should then be washed, dried on filter paper, and weighed. The necessary additional weight of mercury to make a 12.5 per cent amalgam is finally added. It may be kept under cadmium sulphate solution, and should be melted on a water bath to insure homogeneity before using in a cell. This method yields an amalgam free from zinc, and there is no oxide or dross formed, as there is when the amalgam is made by the method of heating the weighed cadmium and mercury.

Mercurous Sulphate.

Recently, both in this country and in Europe, variations in the electromotive force of standard cells have been traced to the mercurous sulphate. The method in use by the European manufacturers of this salt consists in its precipitation by bringing together a solution of mercurous nitrate and sodium sulphate or sulphuric acid. This method does not insure the absence of all nitrate, and when sodium sulphate is used hydrolysis of the precipitated salt takes place. The following standard method has, therefore, been devised by Dr. Hulett:—

In a flat-bottomed glass vessel is placed pure mercury about 2 cms deep. It is covered with dilute sulphuric acid to a depth of 8 or 10 cms. The acid is prepared by adding one part by volume of concentrated H_2SO_4 to six parts of distilled water. Hydrolysis of mercurous sulphate does not take place in the sulphuric acid solution of this concentration. The solution is electrolyzed by making the mercury the *anode* and a piece of sheet platinum hung in the acid the kathode. A current density of about 0.5 ampere per 100 cm^2 surface of mercury may be employed. As soon as the current begins to flow a crystalline mercurous sulphate forms. A stirrer, consisting of a glass rod bent at right angles

at the bottom, must be used to keep the surface of the mercury exposed and to stir the solution and the salt formed; it should be driven rapidly by a motor. A little over 4 grammes an hour can be prepared in this way with a current of half an ampere. The apparatus should be kept covered with black paper or black cloth, since mercurous sulphate darkened by exposure to light gives too high an e.m.f. If the stirring is continued after the circuit is broken, the crystals of mercurous sulphate increase in size and become whiter.

The mercurous sulphate may be removed from the mercury by means of a separatory funnel, but it should be kept under the 1 to 6 acid solution, in contact with mercury, and in the dark.

The Paste.

When ready to fill cells, the mercurous sulphate must first be washed free from sulphuric acid. For this purpose a small Gooch crucible of about 25 c. c. capacity is filled three-fourths full of the salt, avoiding much free mercury which interferes with the filtering. A tiny filter paper covers the perforations in the bottom of the crucible; the whole is mounted on a Bunsen filter flask and the latter is attached to a filter pump.

The mercurous sulphate is first washed a couple of times with the (1 to 6) dilute sulphuric acid, and then five or six times with saturated cadmium sulphate solution to remove the acid; only a few cubic centimetres of the solution are needed for a single washing; after each washing the liquid is to be removed as completely as possible by the filter pump. The last washing leaves the mercurous sulphate ready to be made into a paste. It is advisable to remove the top layer after the last washing.

An alternative method is to wash with absolute alcohol instead of the cadmium sulphate solution, and finally once with sulphuric ether.

The paste is then made in a clean agate mortar by grinding together crystals of the pure cadmium sulphate and a little mercury, and then mixing in about three volumes of the washed mercurous sulphate; finally, add enough saturated cadmium sulphate solution to make a thin paste.

Setting up the Cell.

The *H*-form of cell is altogether the most convenient to make and to fill. Fig. 3 shows the glass cell, ready to

be filled. The tubing is drawn out at *a* so as to leave the diameter about 6 mm and with thin walls at this point. The amalgam is melted over a water bath and is introduced by means of a small tube, slightly contracted at the end, and of a diameter that will allow it to pass freely through the neck at *a*. The warmed tube is used as a pipette, and it permits of introducing the amalgam quickly and without splashing. It should always be wiped with a filter paper or clean cloth before it is introduced into the cell.

The mercury, the thin paste, and the concentrated cadmium sulphate solution may be introduced in the same manner. An

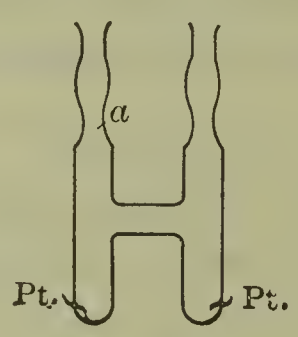


FIG. 3.

alternative method is to fill the cell through little funnels, made by drawing out small test tubes. They must pass through the neck at *a*, and reach well down toward the bottom. After the mercury, the amalgam and the paste have been introduced, both legs of the cell are filled with clean, dry, transparent crystals of cadmium sulphate. Enough of the saturated cadmium sulphate solution is finally added to fill the cell to the top of the cross-connecting tube.

The cell is finally sealed off at the point *a* by means of two small horizontal blast flames, 5 cm long, directed in a line toward each other and just meeting. The narrow part *a* is brought between the impinging flames, the glass quickly softens, and the top part is drawn off. A cell sealed in this way contains nothing but the necessary materials of the voltaic combination. It cannot leak, and can be immersed in a kerosene bath without danger that the oil will penetrate into the inside, as it does when the cell is sealed with paraffin and sealing wax.

RESULTS.

The two curves in Fig. 4 show the behavior of two cells, *D*1 and *D*6, for 40 days after they were placed in a constant temperature bath at 21.1 deg. The lower curve belongs to *D*1 and the upper one to *D*6. *D*6 was made with mercurous sulphate pre-

pared by precipitation with a solution of cadmium sulphate; *D*1 was made with the same materials, except that the electrolytic mercurous sulphate was used. The e.m.f.'s are in international volts.

More than 100 cells in all have been set up to test the various methods of preparing the materials, chiefly of the mercurous sulphate. Many thousands of comparisons have been made. I have

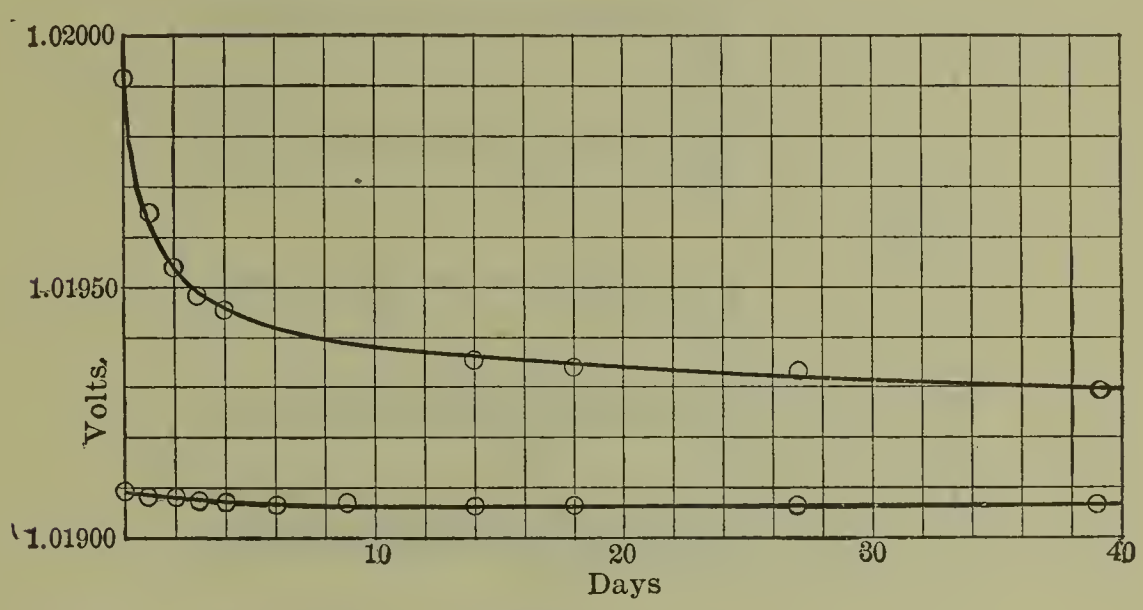


FIG. 4.

selected for the following tables only such as seem to be most valuable from the point of view of the results attained. The comparisons have all been made by means of a potentiometer made by Wolff of Berlin and an H-pattern galvanometer made by the Leeds & Northrup Company of Philadelphia. It is quite easy with this outfit to read to the fifth decimal place. The temperatures were taken with a Haak thermometer, graduated to hundredths and accompanied by a Reichsanstalt certificate.

One cell of Series B, set up in June, 1903, has been used as a reference cell for setting the potentiometer. Six of these *B* cells, set up in the same manner, are in very close agreement. Assuming the ratio Clark 15 deg./Cadmium 20 deg.= 1.40670, the Weston Normal Cell at 21.1 deg., set up with mercurous sulphate made in the old way, would have an e.m.f. of 1.01936 international volts. The values given in the tables are international volts on this basis. All measurements were made with the cells in a kerosene bath; and in every case the temperature was controlled by a thermostat, except for the temperature of 1.7 deg., July 9.

Cells *D*1 to *D*4 were set up Dec. 21, 1903; *F*1 to *F*10, Feb. 15, 1904, the *J* cells and the *K* cells at the date of the first measurements recorded under them.

Date.	D cells.				Date.	F cells.									
	1	2	3	4		1	2	3	4	5	6	7	8	9	10
°					°										
Jan. 5, 21.0	1.01909	1.01910	1.01910	1.01910	Feb. 15, 21.1	1.01907	1.01907	1.01907	1.01908	1.01908	1.019065	1.01907	1.01908	1.01905	1.01907
6, 21.1	08	09	09	09	16, 21.1	065	06	07	08	07	06	06	07	07	065
7, 21.1	08	08	085	09	17, 21.1	07	07	07	07+	07	06	075	075	07	07
9, 21.1	07	08	08	08	20, 21.1	07	07+	075	08	08	08	075	07	08	075
11, 21.1	07+	07	07	08	25, 21.0	08	08	08	08	085	085	08	08	09	08
14, 21.1	07	06	07	075	Mar. 1, 21.1	08	08	08	08+	08	08	08	08	08+	08
19, 21.1	06	065	07	07+	4, 21.2	08	08+	08+	08+	08	08	08	08	08	08—
23, 21.1	06	06	07	07	12, 21.0	075	08	08	08+	08	08	08	075	08	08
Feb. 1, 21.1	065	065	07	075	17, 21.3	075	08	08	08	08	08	08	08	08	08
13, 21.1	07	08	08	085	21, 21.3	07	07+	08	075	07+	07	07+	07+	08—	08
16, 21.1	07	08	08	08	28, 21.0	075	08	08	085	08	075	075	08	08	.....
18, 21.1	07	07	08	08+	Apr. 2, 21.2	07	07+	08	08	08	075	08	08	08+	.....
22, 21.2	07	08+	09	09	9, 21.0	08	08	085	08	09	08	08+	08	08+	.....
25, 21.2	07	08+	085	09	16, 21.0	08	085	085	08+	085	07	08	08	085	.....
Mar. 1, 21.1	07	07	075	08	28, 21.1	07	075	08	08	08+	08	08	08	08	.....
5, 21.2	07	07	075	08	May 13, 21.12	08	085	08	09	09	085	09	09	085	.....
12, 21.1	07	07	07	07+	June 13, 21.16	07	08	08	08	085	08	085	08	.....	.....
15, 21.1	07	07+	07	075	July 9, 1.7	46	51	51	51	52	51	55	51	51	.....
17, 21.0	06	065	07	07+	12, 21.08	08	09	085	09	09	09	085	09	09	.....
Aug. 1, 21.1	05	07	08	08	Aug. 1, 21.08	07	08	08	08	085	08	09	085	085	.....

Date and temperature.	J cells.				Date and temperature.	K cells.						
	3	5	9	10		1	2	3	5	6	9	10
May 13, 21.10°	1.01919	1.01910	.....	.....								
24, 21.05	18	085	.....	.....								
June 6, 21.15	13	11	.....	.....	June 25, 21.10°	1.01919	1.01920	.....	.....	.....	.....	.....
13, 21.16	09	06	.....	.....	28, 21.08	16	16	1.01916	.....	.....	.....	.....
25, 21.10	07	065	1.01914	1.01916	30, 21.00	16	16	15	.....	.....	.....	.....
28, 21.08	07	06	13	14	July 11, 21.15	14	14	13	1.01917	1.01913	1.01918	1.01918
30, 21.00	08	08	14	14	12, 21.07	15	15	15	18	15	17	18
July 27, 21.00	08	09	11	12	27, 21.00	13	14	12	15	14	13	14
August 1, 21.08	06	08	12	12	August 1, 21.08	13	13	13	15	14	13	14

All these cells have been kept for the most part in a bath at about 21 deg.; but the *D* and the *F* series were placed in a bath near 1.5 deg. for 48 hours, or until their e.m.f. had apparently reached a stable value for this temperature. The e.m.f. for the *F* cells at 1.7 deg. are shown in the table under July 9. The *D* cells reached a maximum mean of 1.019625, as compared with 1.01951 for the *F* series. The mean temperature coefficient for all of them for this range of 19.4 deg. is in close agreement with the Reichsanstalt formula.

Of the *J* cells, 3 and 5 contain mercurous sulphate washed with alcohol; 9 and 10 were washed with the $CdSO_4$ solution. All of them are apparently coming down to the level of the *D* and *F* series.

Of the *K* group, 1 and 2 were set up with mercurous sulphate washed with $CdSO_4$ solution; 3, 5 and 6 with alcohol. Cells 9 and 10 were set up with mercurous sulphate prepared with great care by letting mercurous nitrate solution drop, with constant stirring, into a strong solution of sulphuric acid (one gm molecule to a half litre of water). These cells are identical in value with 5 and 6, and they show that it is possible to make mercurous sulphate by precipitation with a strong solution of acid without appreciable hydrolysis, if the proper skill and precautions are applied. But the electrolytic method of preparing Hg_2SO_4 is far easier and the product is much more uniform.

All these *J* and *K* cells exhibit a slow subsidence to their final value. The *D* and *F* series attained their electrical equilibrium very quickly. In fact the first measurements on the *F* cells were made within three hours after they were filled, and they had already attained the values which they have maintained for the past six months.

Discussion.

Doctor R. T. Glazebrook: I think that we all agree that Professor Carhart has advanced very greatly our knowledge of the properties of standard cells by this important piece of work. Similar observations, though not so complete, have been going on for some time in my own laboratory, and we have arrived at very much the same results. For example, we find, as Lord Rayleigh found, that the mercurous sulphate is the chief source of difficulty, and that was made clear in a paper which was read before the British Association a fortnight ago. I there described three methods of preparation, one being that of Professor Carhart, which lead to practically identical results. Without burdening the meeting further with details, I may say that in the results which I have

here for nine cells, prepared by these different methods, expressed in terms of one standard cell, in the same way as in that table, Series F, the numbers that correspond to the numbers given by Professor Carhart would vary between 20 and 21, when expressed in hundredths of a millivolt.

I think it is of importance to observe, as I have stated, that we have reached this result by means of three different methods. Which method may prove to be the most easy in practice or most satisfactory, I am hardly prepared to say at present. I would like to emphasize a point Professor Carhart has made, and which we have found to be the case. It is very necessary to stir well, in using the electrolytic method. We use a rather higher current-density than Professor Carhart recommends. We hope to go on, as I have already stated, as soon as I return, with comparisons between these cells and the electrochemical equivalent of silver. But I have brought with me here to St. Louis six cells prepared in accordance with the three formulas named, and Professor Stratton has promised to have them compared with the Bureau standards and Professor Carhart's cells. It will be extremely interesting to see how far these cells agree as to their e.m.f. Let me say in conclusion, that I think it was a very definite advance to make the cells in the form that Professor Carhart has indicated, and if it is proved, as he has shown in the one case, that these cells will remain for a long time without alteration, then the advance is great indeed.

Dr. H. S. Carhart: Of the two methods of making mercurous sulphate employed at the National Physical Laboratory, the one in which fuming sulphuric acid is used to act on mercury appears to me to be the better. In the other one I should think there might be greater danger of hydrolysis. When the mercurous sulphate is dissolved by heat and the solution is poured into distilled water, the danger is that the water will not contain enough acid to prevent hydrolysis.

Doctor Glazebrook: The method that Professor Carhart has referred to is this: the mercurous sulphate is dissolved in strong acid and then poured into a large beaker containing distilled water. In this way the mercurous sulphate is precipitated down to the bottom of the beaker.

Dr. W. D. Bancroft: The behavior of the mercurous sulphate electrode shows that we have here a reversible electrode. The physical chemists make use of the so called calomel electrode and I should like to call attention to the possibility that this is not a strictly reversible electrode, although we always assume that it is. In some experiments tried in my laboratory with mercury as anode in a chloride solution, we did not get mercurous chloride formed. Instead, there is formed a nonconducting film, probably of oxide. In some other experiments we started with mercury and mercurous chloride as anode in the same solution, and found that mercuric chloride was formed. In course of time this reacts with the mercury. Though I should not care to put much stress on these experiments, it seemed to me there was some evidence that the calomel electrode is not, strictly speaking, a reversible electrode. I hope some one will take the matter up.

The other point I wish to make is, that the distribution of potential difference, on which Professor Carhart lays stress, is of course dependent

on the explicit assumption that the calomel electrode has a single potential difference of 0.56 volt. It is believed by Nernst and Billitzer that this is in error by 0.7 volt. While I have not the remotest idea what the true potential difference is, I am perfectly certain that the flowing electrode does not give the true value. If you determine the value of a chloride electrode and of a bromide electrode and combine these two electrodes to a complete cell, you introduce only the potential difference between the two solutions which can be approximated, and yet you find errors under these circumstances running at least 0.07 volt. Consequently, I feel absolutely justified in saying that 0.56 volt is not the true potential difference of the calomel electrode. In fact nobody knows at present what the true potential difference is.

The CHAIRMAN: We are very fortunate, and very much to be congratulated this morning on having with us an eminent authority on electro-metallurgy, Doctor Héroult, of Paris, and I shall call on him next for his paper on "The Electro-Metallurgy of Iron and Steel."

THE ELECTROMETALLURGY OF IRON AND STEEL.

BY P. L. T. HÉROULT.

The processes that I am about to discuss form, as a whole, a new metallurgical method for the production of iron and steel based on the employment of electrical energy. They are the result of methodical investigations which I have carried on during a long series of years at the works of the Société Electro-Metallurgique Française de Froges, which company has put at my disposal all the resources of its large establishment.

The "siderurgical method" (Froges-Héroult) is clearly distinguished from all the other processes which have appeared either simultaneously or have been inspired by my disclosures, inasmuch as it completely solves the problem, and is based entirely on experimental data. Among the processes heretofore proposed many are only theoretical conceptions, more or less practicable, such as those of Messrs. Harmet and Gin, which never had an existence except on paper.

In their attempts at a solution, some experimenters meet with insurmountable obstacles, and others have put forth only a partial solution of the problem. We should, however, make special mention of the Gysinge process, which furnishes a practicable and elegant solution of the problem so far as relates to the melting of scrap.

I take the liberty of calling to your attention the fact that if one were to judge by the number and extent of the articles that have been published, he would be apt to obtain a false idea of the relative values of the different processes; it seems that those who have written most extensively on this subject are those who have contributed least to its real advancement. Commercial results furnish the best criterion, and from this point of view the Société Electro-Metallurgique Française de Froges is the only company which has, during the last two years, really manufactured and put on the market a complete series of carbon steels of a quality equal to or better than the best tool steel known.

I shall confine myself, however, to the setting forth of my own investigations, and I shall dwell especially upon the sequence of the conceptions and experiments which have led us to develop a method founded exclusively upon the results of actual experiments, completely solving the problem of making crucible steel commercially, and also of improving the quality of ordinary steel at almost no increase of cost.

In the year 1887 I disclosed an electric furnace designed for the manufacture of aluminum which has been accepted as the first continuous commercial electric furnace. In fact, in consequence of its strong construction, and the method of suspending and regulating the electrode, it is adapted to work continuously for a long period of time; and the addition of a tap hole made it a continuous apparatus. Without any modification it has been successfully applied to many different uses. Willson has applied it to the manufacture of calcium carbide. I have myself used this form of furnace in the manufacture of the first commercial carbide made in France; also to the making of artificial corundum, ferro-chrome, and ferro-silicon, all of which, as electrical products, were first put upon the market by the Société Electro-Metallurgique de Froges.

Ferro-chrome made by this process has the same composition as that made in a cupola, except that it is richer in chromium, the metal carbonizing in contact with the carbon walls of the crucible.

Knowing the great interest that the metallurgist would have in a metal containing a small amount of carbon, I modified my apparatus to obtain this result.

The walls of the crucible were made of ferro-chrome ore, and in a receptacle so formed I placed two electrodes which are in contact only with the surface of the slag, or are even above it; the entrance and exit of the electric current is effected at two arcs in such a manner that the metal never comes into contact with the carbon. The reducing carbon being thus exactly proportioned, it is possible to obtain soft metals, that is to say, metals almost entirely free from carbon. This was the first step in the process of the manufacture of steel by the electric furnace.

So far as regards the use of two electrodes in series, I recognized that this arrangement was not new. Mr. Keller had patented it two months before me, and his own patent was anticipated by the patent of Mr. Bullier, taken out in 1895. Besides the use of two electrodes, certain other conditions are to be met in the manu-

facture of steel, and these essential conditions have not been provided for by any of my predecessors.

Moreover, if the double-electrode furnace is the most practicable, it is not the only one by means of which the production of steel is obtainable. I myself patented on Jan. 29, 1901, a furnace with only one electrode, which accomplishes the same result.

From the time that it became possible to manufacture soft metals, it was obvious that steel could be manufactured by the same method, and it became of great interest to the manufacturer to know that a large electric furnace could be employed for this work, and the inconveniences of blast-furnaces, puddling-furnaces, converting-furnaces, pot-furnaces, etc., could thereby be eliminated. I was attracted at the outset by the idea that I could, in fact, reduce iron ore in my double electrode furnace, the product of the reduction containing only a small percentage of carbon, and then could increase the percentage of carbon to the desired quantity.

It became evident that it was not advantageous to perform all these different operations, namely, the reduction of the ore, the oxidation, recarbonization, etc., in one and the same apparatus. We were, therefore, led to divide it into two parts, and make pig-iron in a special electric crucible. This operation takes place without any special difficulty, providing the indispensable precautions be taken in the arrangement of the charge and in carrying out the operation. In a general way it is not advantageous to transform electrical energy into heat for the reduction of an ore so easily reducible as that of iron. As electric heat is very costly, it must be economized to the fullest extent.

There are two means of economizing this electric heat; one is my patented device called the "Economizer." That device is based upon the principle of combining the total amount of oxygen contained in the ore with carbon to CO. This CO is subsequently burnt by admitting the necessary amount of atmospheric air. The heat generated in this last operation is used to heat the ore previous to its reduction. As a matter of fact the ore falls into the reduction chamber in the molten state. The amount of electrical energy necessary for carrying out the operation is theoretically nil, although in the experiments made in practice it amounted to quite a considerable quantity on account of losses due to radiation. This process did not prove entirely satisfactory owing to the great difficulty of preventing the walls from corroding, and also to the consumption of the reducing carbon, which is large.

The second process, which has always been successful, consists in reducing one-half of the ore in the molten state, while the other half is reduced in the solid state by means of the CO evolved by the first half. If one makes the calculation of the heat units absorbed by the reduction and the heat units evolved by the burning of the carbon in the form of CO^2, he will see that the quantity of electrical energy needed is very small.

I will not discuss further the manufacture of pig-iron, because the electric process, although very interesting, is applicable only under certain conditions and is not likely to supersede the blast-furnace in localities where coal is cheap and is the only source of energy.

I will now proceed to discuss the electrical steel process. This process, which is operated at La Praz in France and at Kortfors in Sweden, produces steel of a quality equal to and superior to the best crucible cast steel. The quality of the raw material from which it is made is a matter of indifference. For instance, steel containing less than .01 sulphur and .01 phosphorus is being made from raw material like scrap, which contains .15 sulphur and .30 phosphorus. The electric furnace has enabled the metallurgist to get rid, once for all, of the necessity of choosing beforehand his raw material and paying a high price for it. The dephosphorising of metals was well understood, although the facilities afforded by the electric furnace are such that it was rendered possible to attain in one operation the results above referred to. The process of desulphurization, which up to the present time has always been considered unsafe and erratic, has been brought to a high degree of perfection. I have discovered the reasons for this erratic behavior involved in the desulphurization of steel, and by means of the electric furnace we have the entire operation under perfect control. We can regulate the temperature as we choose and carry out the work without any oxidation by the air.

I make the claim that at a cost not exceeding half a dollar a ton, I can make out of any steel delivered in the molten state, that is, as tapped out of a Siemens furnace, or from the Bessemer converter, a metal of any desired composition containing less that .01 sulphur and .01 phosphorus. It is evident that the electric process must not be considered as a steel-making process, but as an adjunct to existing plants and apparatus. By means of this electrical adjunct, the commercial value of the product has been greatly increased. It is obvious that there is a great advantage in using a metal free from

impurities, such as sulphur and phosphorous, and the day will come when the requirements of the public and the specifications of government contracts, railroads, etc., will be such that the iron-masters will have to furnish material thus purified and answering these conditions. They will have no excuse for not doing so, because there is now put at their disposal a cheap method of accomplishing the desired result. I am far from predicting that the electrical furnace process will supersede the older metallurgical one, but it will and must cause a revolution so far as the quality of the metal used in the industry is concerned.

Discussion.

Prof. J. W. Richards: I have listened with great interest to Doctor Héroult's paper, because I know he is in the forefront of those who are beginning this method of manufacture of steel. The manufacture of the higher grades of steel has been the only available point of attack, because of the present cost of electric manufacture, but the manufacture of these high grades is now a commercial success. The advantages of electric manufacture are so great, especially in view of the inevitable advances which are going to take place in the development of electric furnaces in the next five or six years, that I have no doubt that the larger part of the fine steel consumed is going to be made in this way. When we consider that the finer grades of steel, such as armor plate and steel for guns, is sold at several hundred dollars a ton, the increased cost of the electric manufacture of the raw material—provided it gives a material lower in sulphur and phosphorus and free from nitrogen—is negligible. The greatest development of this manufacture in the near future will be in the commercial grades of steel, such as soft steel. I do not think it impossible that within a few years there will be a large steel industry in Canada, where pig iron is cheap and where there are all inducements for setting up an electrical industry. A few years more, and I think it will find a place in the United States, where it will probably be used as an adjunct to the open-hearth furnace. For temperatures up to the melting point of pig iron, it is probable that the use of producer-gas and the ordinary furnace will always be most economical; but for the additional 500 degrees necessary to reach to the melting point of steel, the electric furnace is, I believe, even under present conditions, the more economical of the two apparatus, and the combination of the gas furnace with the electric furnace will, I believe, be the next subject of development in the electro-manufacture of steel. I think we are in a period of transition, and that this is the beginning of a great commercial revolution in the manufacture of this most important product.

Mr. E. H. Whitlock: From the manufacturer's side of the question I would like to ask what current-density is used in the electrodes, and whether it is desirable for this to remain about what it is at present? I had the privilege of visiting a plant in West Virginia some time ago,

and at that point they required something like 125 amperes per square inch, which seemed to be rather excessive.

Mr. W. McA. Johnson: I have listened to the paper of Doctor Héroult with great interest. Any one connected with the operation of large metallurgical works is forced to the conclusion that there is a vast difference between the writing of a paper on the probable success of a process and the actual working of that process on a large scale. A point which I shall try to bring out in my paper tomorrow is this, that the best criterion of a new process is the actual production of the finished material. Right here is where Doctor Héroult's work is to be admired.

The second point which this paper of Doctor Héroult has elucidated and which is one of a few general principles to be given in my paper, is the principle that the electric current can be best used by the metallurgist for the finishing of metallurgical work. This principle was first called to my attention by Col. Robert M. Thompson, formerly president of the Orford Copper Company, and Mr. Victor Hybinette, superintendent of the same company, when I was in its employ. The principle is a very general one. Tomorrow I will try to give a few of its applications to the metallurgy of this country, as far as I have seen it. But both of these ideas are better illustrated by this paper than I can hope to do.

The following paper was then read by Mr. S. E. Whiting:

THE PRESENT STATUS OF THE EDISON STORAGE BATTERY.

BY DR. A. E. KENNELLY AND MR. S. E. WHITING, *Harvard University.*

The following paper is presented on behalf of Mr. Thos. A. Edison, as a brief synopsis of the results obtained with his storage battery up to the present date.

History.

About 1898, Mr. Edison began seriously to investigate alkaline storage cells. After trying a very great number of combinations, the nickel-iron couple became fairly well developed in 1900.

The first type of cell put into service in vehicles was named Type C. This was an 18-plate cell (9 of iron and 9 of nickel), weighing complete 17 1/2 lbs. (7.95 kilos). At 20 amperes discharge (9.5 hours) to 0.75 volt the average potential difference was 1.23 volts and the quantity 191 amp-hours representing 234.9 watt-hours or 13.4 watt-hours per lb. (29.6 watt-hours per kilo). At 120 amperes discharge (1.4 hours) to 0.75 volt, the average potential difference was 1.03 volts and the quantity 171 amp-hours, representing 176 watt-hours or 10.06 watt-hours per lb. Several hundred of these cells were made up and are still in use in vehicles at the factory.

This Type C cell was not regarded as entirely satisfactory because it did not promptly recover its full normal voltage after heavy rates of temporary discharge. This seemed to indicate an inadequate circulation of electrolyte in the cell and pointed to a reduced current density; i. e., to a larger plate-surface for the same mass and volume of active material. The improvement required new tools and months of delay, but was nevertheless undertaken, and the new cell developed was named Type D.

The type of D cell was first completed in May, 1903. It was a 28-plate cell (14+ and 14—) weighing 17.8 lbs. (8.05 kilos) and occupying the same space as the 18 plates of Type C, thus providing

an increase of about 50 per cent in active surface with a corresponding reduction in briquette thickness, to the improvement of circulation.

Tests of the Type D cell were made not only at the Edison laboratory but also by several independent experimenters both in this country and in Europe. These tests will be referred to later. The factory tests of Type D showed at 20 amperes discharge (8.45 hours) to 0.75 volt, the average potential difference of 1.28 volts and the quantity 169 amp-hours, representing 216.5 watt-hours or 12.18 watt-hours per lb. (26.9 watt-hours per kilo). At 120 amperes (1.38 hours), to 0.75 volt, the average potential difference was 1.17 volts and the quantity 165 amp-hours, representing 193 watt-hours or 10.85 watt-hours per lb. (24 watt-hours per kilo). The corresponding internal resistance is 0.0013 ohm.

The change from Type C to Type D had succeeded in enabling the cell promptly to return to its normal e.m.f. after temporary heavy discharges, and improved the output under heavy discharge from 10.06 to 10.85 watt-hours per lb. (22.2 to 24 watt-hours per kilo). On the other hand, the output at low rates of discharge had somewhat suffered by the change, and the new cell was also found to be somewhat unbalanced in the individual capacities of the + and — plates, there being an excessive capacity in the iron plates.

A further modification was, therefore, made in the cell, resulting in the production of Type E, the latest type.

Types C, D and E have the same height, length and general external appearance and differ externally only in their breadth. Type E is the cell now manufactured and placed on the market in three sizes, which differ only in the number of assembled plates. The cell of Type E tested by the author's and here considered is E-18, having 12 nickel plates and 6 iron plates. The weight of the E-18 cell complete is 12.66 lbs. (5.75 kilos). The normal rated delivery of these cells is 114 amp-hours, which is practically the same at either the 30-ampere or 120-ampere discharge rate. At the 30-ampere rate (3.8 house), the mean potential difference to 0.75 volt is 1.234 volts, representing an output of 141 watt-hours or 11.1 watt-hours per lb. (24.6 watt-hours per kilo). At the 120-ampere rate (0.95 hour), the mean potential difference to 0.75 volt is 1.04 volts, representing an output of 118.5 watt-hours or 9.38 watt-hours per lb. (20.7 watt-hours per

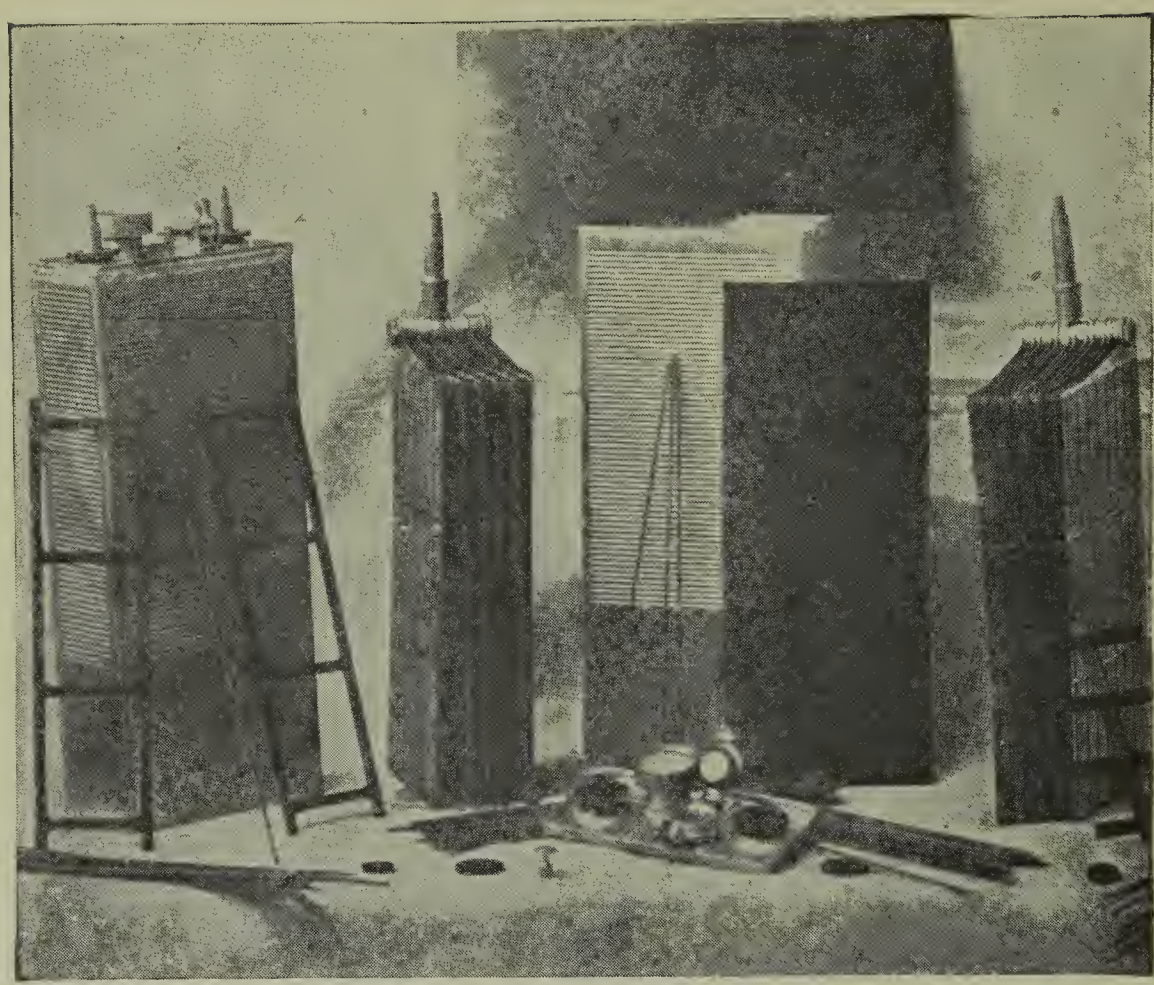


Fig. 1.—Parts of edison storage battery.

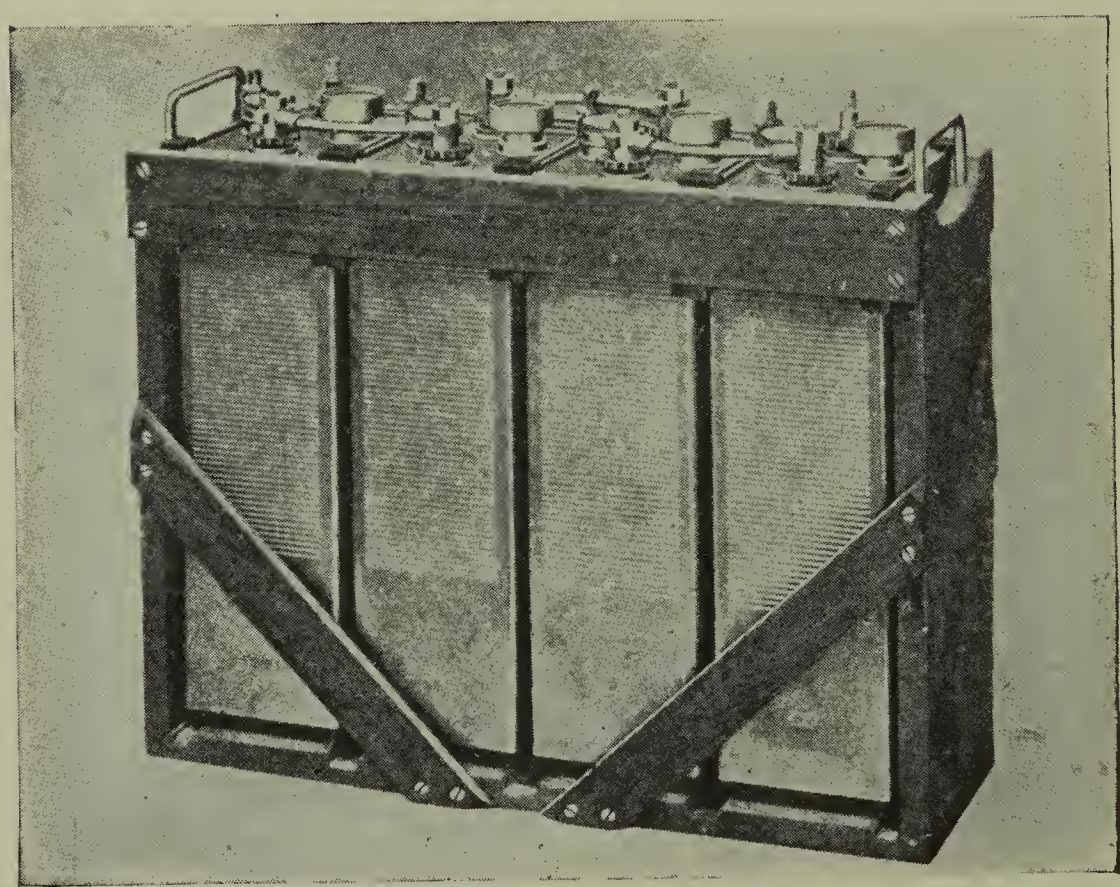


Fig. 2.—Edison storage battery.

kilo). Although the above are the normal rated capacities, the full capacity of the cell is found to be about 140 amp-hours, which makes the total output at 30 amperes, 173 watt-hours and at 120 amperes 145 watt-hours; or the specific output 13.7 watt-hours per lb. (30.2 watt-hours per kilo) and 11.5 watt-hours per lb. (25.4 watt-hours per kilo) at the two rates respectively.

Construction of Type E.

The construction of the cell is shown in Fig. 1 which exhibits the various parts both separate and assembled. The containing cell, as also the grids and pockets, are made of thin sheet-steel plated by a special process. The jar completely encloses the element and the lid is soldered permanently in place. There are four openings in the steel top. Two of these are insulated by rubber bushings through which the terminal posts project. The third opening is a filler-hole with gas-tight hinge-stopper. The fourth opening is a gas-vent provided with a valve and gauze screen to prevent escape of entrained liquid.

The insulation between the walls of the can and the enclosed element is all of hard rubber. On the bottom is the four-barred grating, seen on the right-hand side of the figure, and 0.4 in. (10.2 mm) deep. On the ends are ladder-like frames giving about 0.11 in. (2.8 mm) clearance and grooved to hold the edges of the plates. On the sides are solid sheets 0.014 in. (0.56 mm) thick. It has been found necessary to subject all the rubber insulation to a special chemical treatment to prevent a foaming action on the alkaline electrolyte.

Between the plates are threaded four-cornered rods of rubber about 0.1 in. (2.5 mm) thick and spaced 0.57 in. (14.5 mm) apart. The distance between opposed plate surfaces is about 0.04 in. (1 mm).

Plates of like polarity are bolted to a horizontal-bar at the top provided with spacing washers and joined to the vertical terminal post.

For use in vehicles the cells are grouped in wooden trays (Fig. 2) containing 3, 4 or 6 cells each. Connections between cells are ingeniously made by taper lugs and each jar is insulated from its neighbors and from the base by spacing blocks and a rubber pad, respectively.

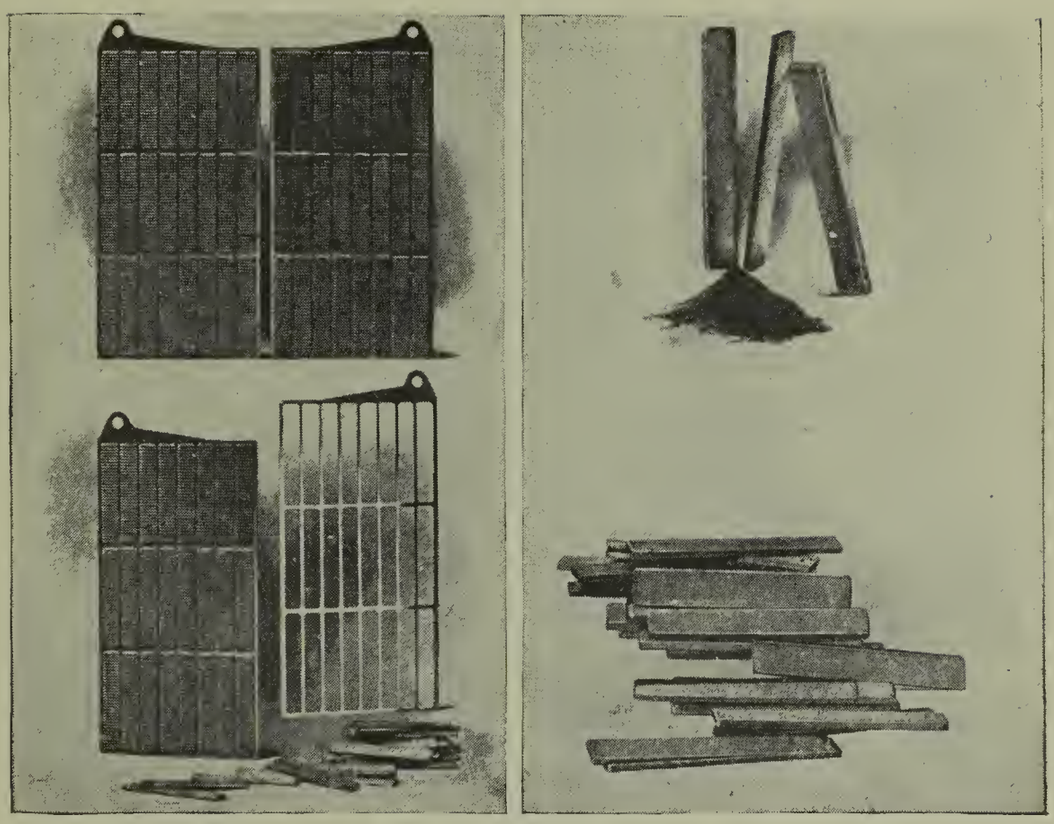
The grid itself, Fig. 3, and the pockets containing the active materials are identical for both positive and negative electrodes. The grid is 9.25 in. high (235 mm) — excluding the lug — 4.75 in. (121 mm) wide and 0.015 in. (0.38 mm) thick. It contains 24 rectangular holes, each 2.95 in. (.75 mm) high and 0.5 in. (12.7 mm) wide. Into these holes are fitted the pockets illustrated in Fig. 4. These are made up of strips of 0.003 in. (0.076 mm) steel, having flanged edges that telescope together to form the pocket or container of the active material. These pockets have each about 5000 perforations.

The active material of the positive plate is an oxide of nickel in finely-divided form commingled with a conducting substance such as flake graphite, in order to improve the conductivity of the mass. The active material of the negative plate is finely divided iron similarly commingled with a conducting substance. The electrolyte is a 20 per cent aqueous solution of potassium hydrate.

In assembling, the pockets are filled with active material, closed and inserted in the holes of the grid. The plate is then subjected to a pressure of 150 tons for the purpose,— first, of flanging the pockets over the holes in the grid, in order to lock them firmly in position; and second, of corrugating the surface of the pocket, in such a manner as to provide adequate elastic movement of the envelope in view of the contraction and expansion of the contents.

The weight of the active material in its initial condition and including the conducting material is about 3.2 grammes per pocket for the nickel and 4.6 grammes for the iron plate. This represents a total quantity of 922 grammes positive active material, and 662 grammes of negative active material in an E-18 cell. The weight of electrolyte per cell is 3.1 lbs. (1.40 kilos) at a normal density of 1.190, which represents about 25 per cent of the total weight of the cell.

The cell is at present manufactured in three sizes stated in the following Table:



FIGS. 3 AND 4.—DETAILS OF EDISON STORAGE BATTERY.

Type.	Positive plates.	Negative plates.	Capacity in ampere-hours.		Normal charging current.	Normal charging time.	Weight complete.		Dimensions over all (excluding trays).							
									Length.		Breadth.		Height.		Volume.	
			Normal.	Maximum.	Amp.	Hours.	Lbs.	Kilos.	Ins	Cms.	Ins.	Cms.	Ins.	Cms.	Cu. ins.	Cu.cm.
E-18.....	12	6	110	140	40	3.75+	12.5	5.66	5.	13.0	2.6	6.6	13.2	33.5	175	2,874
E-27.....	18	9	165	210	60	3.75+	17.5	7.95	5.1	13.0	.....	.....	13.2	33.5	.....	.....
E-45.....	30	15	275	350	100	3.75+	30.0	13.6	5.1	13.0	.....	.....	13.2	33.5	.....	.....

Chemical Theory.

The Edison cell is of the oxygen-lift type. That is to say, the process of charging consists in driving oxygen electrolytically from the negative to the positive plate. During discharge the oxygen leaves the positive plate and enters the negative plate. The chemical actions in the cell have not, as yet, been completely investigated.* The following conditions may, however, be accepted provisionally as forming a working theory:

Condition.	Positive plate.	Electrolyte.	Negative plate.
Charged.....	NiO_2 NiO_2	KOH H_2O KOH	Fe
Discharging ..	NiO_2 $\overset{+}{K}$ NiO_2 $\overset{+}{K}$	H_2O	$\overset{-}{HO}$ $\overset{-}{HO}$ Fe
" ..	$+Ni_2O_3$ KOH KOH	H_2O	FeO—
Discharged....	Ni_2O_3	KOH H_2O KOH	FeO

The cycle represented in the above table shows that during discharge the electrolyte divides into potassium cations and hydroxyl anions, the former being directed toward the positive plate and the latter toward the negative plate. On arriving at these plates the ions give up their respective charges. At the positive plate, the potassium robs the nickel oxide of a portion of its oxygen and, in combination with the water present, forms new molecules of potassium hydrate, the original electrolyte. At the negative plate the hydroxyl ions deliver oxygen to the ion and form water. Thus the electrolyte tends to become concentrated in the pores of the positive plate, and attenuated in the pores of the negative plate. Diffusion ultimately destroys this difference of concentration and leaves the electrolyte in its original condition, since at any instant the total quantity of water and of potassium hydroxide (including the pores of both plates), remains the same.

* E. F. Roeber. *Transactions* A. E. S. Vol. 1, 1902. M. V. Schoop, *Electrochemical Industry*, July and August, 1904.

It would appear from the form of e.m.f. curve during complete discharge, as shown in Fig. 5, that after the cell has become almost entirely discharged other stages of oxidization develop, and further investigation may show that the outline of the chemical cycle above presented is very incomplete. Whatever the complete cycle may be, it is, in all probability, however, of the type indicated.

It would seem that neither the plates of nickeled steel nor the active materials within them are subject to local or chemical corrosion, or solution, in the electrolyte of potassium hydroxide. For this reason the cell is chemically stable either in the charged, discharged or any intermediate condition.

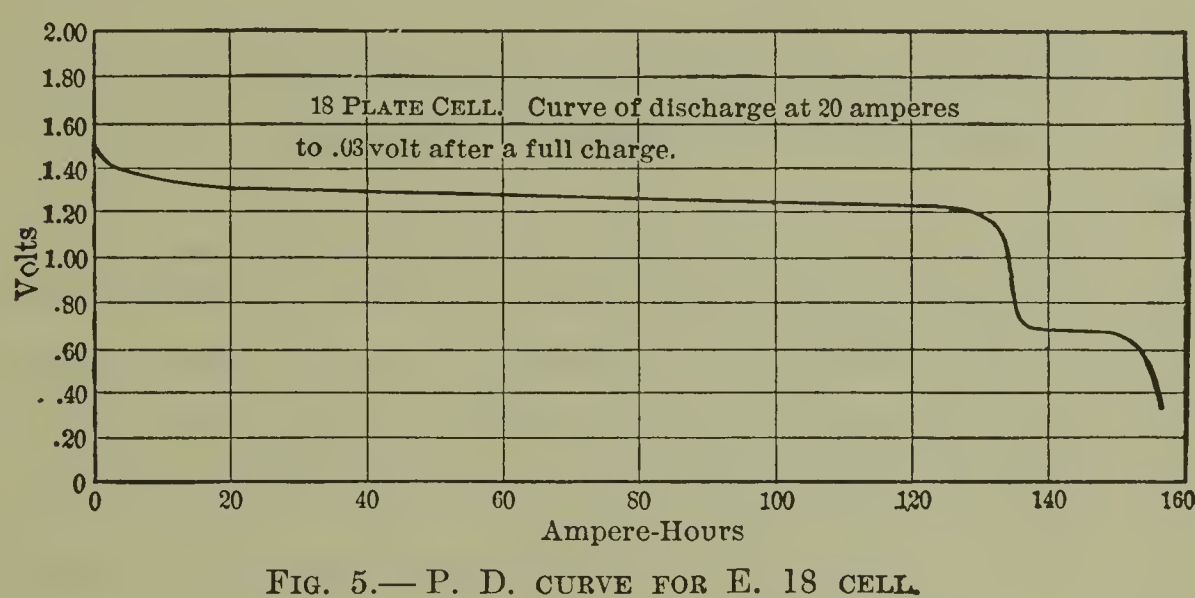


Fig. 5.— P. D. curve for E. 18 cell.

Electrical Theory.

Electromotive Force.

Various observations both of the authors and other observers show that the discharge curve of e.m.f. of the Type E cell possesses the following peculiarities:

(1) An initial period of rapid descent occupying about 10 per cent of the delivery period.

(2) A nearly steady gradient of gradual descent continuing until within about 10 per cent of the end of the whole delivery period.

(3) A final period of rapid descent occupying the last 10 per cent of the delivery period (assumed as stopping at a potential difference of 0.75 volt).

A fair sample of this curve is represented by the heavy line *a b c d* in Fig. 6, where *ab* is the initial descent, *bc* the nearly uniform descent, and *cd* the final rapid descent. The initial

e.m.f. at *a* is influenced by the previous history of the cell, more particularly by the time which has elapsed since the close of the preceding charge. The range of initial e.m.f. is between 1.35 and 1.65 volts. It would seem that this e.m.f. depends upon the amount of gases remaining after the charge, occluded in the pores of the cell.

The e.m.f. at and near the end of the discharge is also somewhat variable, depending in some measure upon the rate and nature of the discharge. It clearly accompanies the exhaustion of the active materials.

Between the points *b* and *c*, the gradient of descent is substantially uniform and approximately independent of the discharge rate within the usual working limits. This diminution of e.m.f. may possibly be due to the increasing thickness of the layer of effete material formed by the progressive exhaustion of the active material.

If the curve *a b c d* be integrated, the mean ordinate is found closely to approach the actual ordinate at *C* or the point of half delivery. This means that a straight line *A C D* may be chosen nearly coinciding with the steady gradient of the actual curve *bc*. This is shown in a dotted line *A C D* in the figure. The area above this line *A a b* at the beginning is approximately equal to the area below the line *c D d* at the end. These areas represent, therefore, sensibly equal and opposite quantities of electrical energy, with respect to the curve *a b c d*. Consequently, we may for practical purposes replace the actual curve *a b c d* by the equivalent straight line *A C D*, which is represented by the formula

$$e = 1.37 - \frac{x \times 0.14}{100} \text{ volts}$$

where x is the percentage already yielded, of the full delivery. The mean discharge e.m.f. is, therefore, 1.30 volts. This approximation greatly simplifies practical computation with the Edison battery.

Internal Resistance.

It has been observed both by the authors and by other experimenters that the internal resistance of an Edison Type E cell is substantially constant during the main working portion of the discharge corresponding to *bc* in Fig. 6. Thus in the E-18 cell, the internal resistance at ordinary temperatures is about 0.0022 ohm. This would correspond to 0.0278 ohm in a Type E similar cell

weighing 1 lb.; or to 0.0126 ohm in a cell weighing 1 kilo. The internal resistance is slightly less at the beginning of the discharge, but becomes considerably greater near the end of the discharge. Since, however, this rise in resistance occurs only during a small portion near the end of the delivery, its effect in the total discharge may be neglected for most practical purposes.

The internal resistance does not vary greatly with the discharge rate within the usual working limits of 0 — 150 amperes. In other words, the drop of pressure in the cell is approximately proportional to the discharging current strength.

Power.

The maximum amount of power obtainable in the external circuit of any cell is $\frac{e^2}{4\,r}$ watts; where e is the actual e.m.f. and r the actual internal resistance of the cell. Under these conditions the cell will work at 50 per cent efficiency, with equal internal and external resistance. In other words, it is impossible to obtain from any cell a greater amount of external power than corresponds to the above expression, which represents the maximum power of the cell. Taking the mean e.m.f. of the Edison Type E-18 cell as 1.3 volts and the internal resistance as 0.0022 ohm, the maximum power is 192 watts or about 1/4 horse-power or 15.15 watts per lb. (33.4 watts per kilo) at a current strength of 296 amperes, corresponding to a discharge time of less than one-half hour. We have taken a current averaging 250 amperes from such a cell on approximate short-circuit (through heavy leads and an ammeter) for a period of 30 minutes.

The practical rate of power delivery at 150 amperes is $\{1.3 - (150 \times 0.0022)\}\ 150 = 145.5$ watts, or 11.5 watts per lb. (25.4 watts per kilo). This is on a par with the full-load output of good dynamo machines.

Energy.

The energy liberated in an Edison E-18 cell is 1.3 volts $\times$ 141 amp-hours $=$ 183.3 watt-hours $=$ 14.48 watt-hours per lb. (31.9 watt-hours per kilo) and this liberation of energy is constant to a first approximation for all rates of discharge within the working limits. The amount of this liberated energy which is delivered in the external circuit depends only on the electrical efficiency of

the circuit, or on the drop of pressure in the cell. Thus, at 90 per cent electrical efficiency, or 10 per cent internal drop (corresponding to about 60 amperes in the E-18 cell), the externally delivered energy would be $183.3 \times 0.9 = 165$ watt-hours.

It can be shown that if any Edison Type E battery, in any grouping of cells, be discharged at the rate of p watts per unit mass, reckoned at the mean voltage of discharge, the electrical efficiency, η, of the battery circuit will be $\eta = \frac{1 + \sqrt{1 - n}}{2}$, where $n = \frac{p}{P}$ and P is the maximum power per unit mass or $\frac{e^2}{4mr}$, where m is the mass of a cell.

Thus if a battery of 68 Edison Type E-18 cells be discharged at 120 amperes or 124.3 average external watts, the total external power will be $68 \times 124.3 = 8454$ watts, and the total weight being 861 lbs., the power rate per lb. taken from the battery is 9.83 watts. The maximum power rate is, however, 15.15 watts per lb. as above; so that the ratio $n = \frac{9.85}{15.15} = 0.65$. The electrical efficiency of the battery circuit is, therefore,

$$\eta = \frac{1 + \sqrt{1 - 0.65}}{2} = 0.796$$

or 79.6 per cent. The delivery per lb. of battery will, therefore, be $14.5 \times 0.796 = 11.5$ watt-hours per lb., and the entire battery will deliver 9900 watt-hours to the external circuit, when discharged to 0.75 volt P. D. per cell. The same formula applies to *all* batteries capable of maintaining definite values of e and r under load.

Charging Conditions.

Electromotive Force.

The charging e.m.f. of an Edison cell is approximately 1.6 volts (somewhat greater at the outset) until about 60 per cent of the charge has been stored, when it rises to about 1.75 volts, simultaneously with increased evolution of gases. This rise is, therefore, apparently connected with gaseous polarization. To the e.m.f. of the cell must be added the drop in internal resistance, in order to find the potential difference at charging terminals. The mean e.m.f. of the cell during charge may, therefore, be taken as roughly 1 2/3 volts. The resistance of the cell during charge is approximately the same as during discharge, being greater at the outset

of the charge, corresponding to the condition of resistance at the end of the discharge.

Gassing.

During the charge of Edison cells, bubbles of gas are liberated at both plates, oxygen at the anode or positive plate, and hydrogen at the cathode or negative plate. The collected gases form an explosive mixture. In the ordinary charging process there is a distinct evolution of gas at the outset which reaches its maximum in about a quarter of an hour. The gassing then decreases to a lower steady value which continues until about 60 per cent of the charge, after which it rapidly rises to a steady much higher value than at first. The electrical energy expended in the liberation of these gases is practically all lost.

To replace the water thus lost by decomposition during charging, a small quantity of distilled water has occasionally to be added to the cells through a filler conveniently adapted to this purpose.

Efficiency.

Since the mean e.m.f. of discharge is approximately 1.3 volts, and the mean e.m.f. of charge approximately 1.67 volts, it follows that the superior limit of watt-hour efficiency in an Edison cell is $\frac{1.3}{1.67}$ or 78 per cent. In practice it is always less than this, due to internal drop.

The efficiency may best be examined first in relation to the voltage of charge and discharge, and second, in relation to the electric quantity charged and discharged.

1. If there were no drop of pressure due to internal resistance, either in charging or in discharging, and all the electricity charged in the cell (as expressed in coulombs or amp-hours) were discharged, the amp-hour efficiency of the cell being thus 100 per cent, the watt-hour efficiency would be 78 per cent or thereabouts. This figure can, in fact, be approached by employing very low rates of charging and discharging; i. e., by taking many hours to each process. On the other hand, the more rapid the charge and discharge, the greater the IR drop in the cell, and the less the efficiency, even on the assumption of 100 per cent amp-hour efficiency. Thus at 60-amperes charging and discharging rates, the potential difference in charge would average about 1.8 volts in the E-18 cell and the potential difference in discharge would average about 1.17

volts to the 0.75 volt limit, representing a watt-hour efficiency of 65 per cent, with 100 per cent amp-hour efficiency.

2. The Edison cell would manifestly possess an amp-hour efficiency of 100 per cent if no gases or irreversible substances were generated in its cycle of chemical action. Thus if a certain number of grammes of ion were reduced and a certain number of grammes of nickel were oxydized by one ampere-hour of charging current, and no other action took place, then on discharge the reconversion of these masses of active material would develop the complete ampere-hour of electricity. On the other hand, every gramme of hydrogen (or the equivalent mass of oxygen) liberated and discharged from the negative plate during charge absorbs 26.8 amp-hours of electricity, which is not returned to the circuit during discharge. The amp-hour efficiency of the Edison cell is, therefore, determined by the amount of gas escaping during the charge. This in turn depends upon the rate of charge, or charging-current strength, since the greater this strength the greater the drop in internal resistance, and the sooner the plates are brought to that difference of potential at which the water is rapidly decomposed.

At high rates of charge, then, the watt-hour efficiency of the cell must fall off, not only because of the voltgage drop, but also on account of the reduction of amp-hour efficiency in gasification.

Nevertheless, in many cases, and particularly in automobile work, this sacrifice of energy is amply warranted by the convenience and saving of time effected by rapid charge. The normal charging time of Edison E cells is about four hours. In cyclical charges and discharges of four hours each, the amp-hour efficiency is about 75 per cent and the voltage ratio 70 per cent, so that the watt-hour efficiency may be taken in round numbers as 50 per cent ($0.75 \times 0.7 = 0.525$). It is possible, at a still greater sacrifice of efficiency, to charge the cell at fully double the above normal rate.

Tests.

Laboratory Tests.

Tests of the various types of Edison cell have been made in great numbers and in great variety at the Edison laboratories. Tests have also been made in Europe on Type D cells and published near the end of the year 1903 by Finzi and Soldati at Milan (Associazione Elettrotecnica Italiana, 12th October, 1903), by M. E. Hospitalier at the Central Laboratory of Electricity in Paris (*L'Industrie Elec-*

trique, pp. 493–497, November, 1903), and by Mr. W. Hibbert and Dr. J. A. Fleming, in London (*Journal* of the Institution of Electrical Engineers, Vol. 33, No. 165, April, 1904, pp. 203–238). The authors also have conducted at Harvard University a number of tests on cells of Types D. and E. All of these tests are fairly concordant and in conformity with the data given in this paper.

The essential results of these various tests are represented in the accompanying chart, Fig. 7. This chart gives the output of the Edison cell (per unit mass) at varying power rates of discharge. Curves I, II and III represent the laboratory tests obtained for Type D by the Laboratoire Central d'Electricité, Mr. Hibbert and M. Hospitalier, respectively. Curve V represents the corresponding values for the E-18 cell on normal-rated capacity and delivery. Curve IV represents, on the other hand, the corresponding values

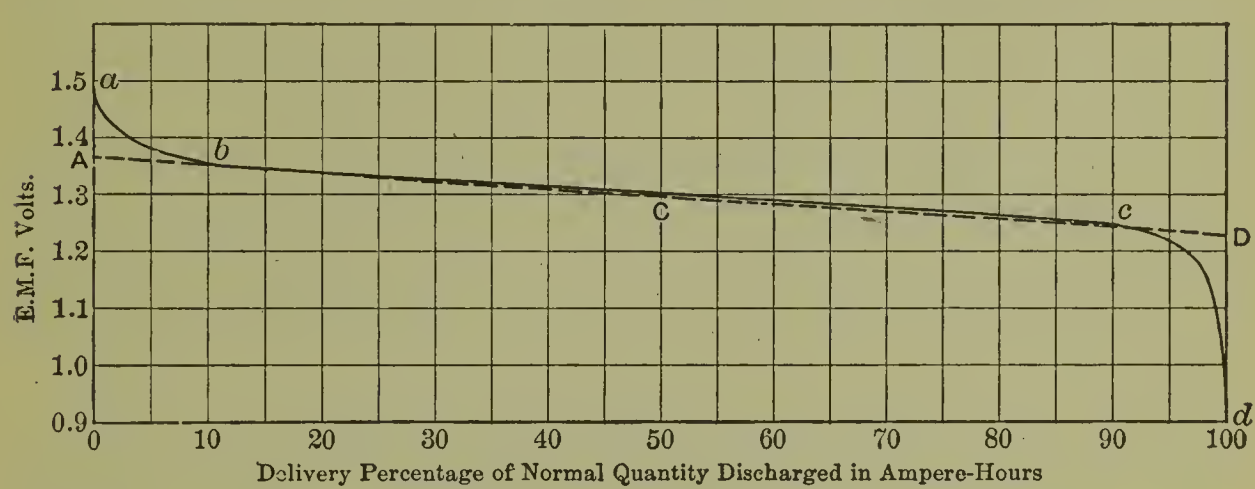


FIG. 6.—ACTUAL AND EQUIVALENT E.M.F. CURVES DURING DELIVERY.

for the E-18 cell, when operated under laboratory conditions of maximum capacity and delivery. In practice, the output may be expected to fall between these two curves, IV and V.

Although the authors' tests of the Type E cell have been confined to the E-18 12 1/2 lb. cell, factory tests of the larger sizes of this latest show about 12 per cent greater maximum output per unit mass than corresponds to Curve V. This may be accounted for by the lesser proportion of dead weight (solution, jar and connections) than is presented in the E-18 cell.

Automobile Tests.

Much experience has been attained in actual service from the Edison battery on automobiles. This experience has led to the elimination of some of the minor practical difficulties that any new battery always encounters. The successive improvements in the

battery have, in fact, been due to the perception of defects discovered in actual vehicle practice.

Mr. H. M. Wilson of the Boston Edison Illuminating Company reported some observations on an Edison automobile battery of 68 D-28 cells regularly employed in a single-seat service wagon of the Boston company carrying two persons. The weight of the battery was 1260 lbs. (570 kgs). In four rows of 17 cells each, it occupied a space (including trays and lugs) of about 6 ft. x 2 ft., and was about 1 1/3 ft. high, thus having an over-all volume of 16 cu. ft. (0.45 cu. meter). The weight of the vehicle complete was about 3150 lbs. (1425 kgs). During 22 working days of regular urban service in October and November, 1903, the battery received 1380 amp-hours at 110 volts, or 151.4 kw-hours; and delivered at terminals 68.85 kw-hours at an average potential difference of 85 volts. The amp-hour efficiency was 58 per cent, the volt efficiency, 77 per cent, and the watt-hour efficiency, 45 per cent. The distance run was 324 miles, or 14.7 miles daily, and the energy consumed per mile was 0.47 kw-hour. These results are not only much surpassed by similar batteries of type E, but they are also stated to be exceeded by later batteries of the type D here referred to. Consequently, these results may be regarded as conservative.

Durability and Depreciation.

It would seem that the Edison cell is so durable that no electrical depreciation is discernible in the cells during the three years' total experience of the practical construction of the battery. No mechanical corrosion of the plates or pockets has been discernible during that time and no depreciation seems to have yet occurred in the active material, judging from the capacity tests of cells which are stated to be as great at the present time as they were when the cells were first constructed. The authors have recently confirmed this observation in the case of Type D cells that have run nearly 3000 miles in an automobile of the Edison Company in Boston. The capacity of these cells was found to be equal to that of new cells of the same type. Two of these cells were opened for examination and the sediment in them collected and dried. The dry sediment weighed 3.9 and 7.1 grammes respectively, probably less than one-third of 1 per cent of the active material in the grids. In fact, a new cell freshly set up will show about this quantity of material washed by the solution from the external surface of the plates. No

signs of depreciation or corrosion appeared on any of the plates or connections.

Effect of Rest.

According to observations at the factory, Edison cells lose 15 per cent of their amp-hour charge in eight weeks of idleness. Another test showed 11 per cent of loss by standing one week. Hibbert's tests on Type D showed 9 per cent loss in 48 hours and 27 per cent in 26 days. Hospitalier's tests on Type D showed less than 10 per cent loss after 24 days. A test of the authors on four Type E-18 cells gave, after 26 days' idleness, 100 amp-hours per cell. This represents a loss of 9 per cent of the normal-rated capacity of the cells or 28.6 per cent of the maximum-rated capacity. At a corresponding charge the delivery within 24 hours would have been about 140 amp-hours.

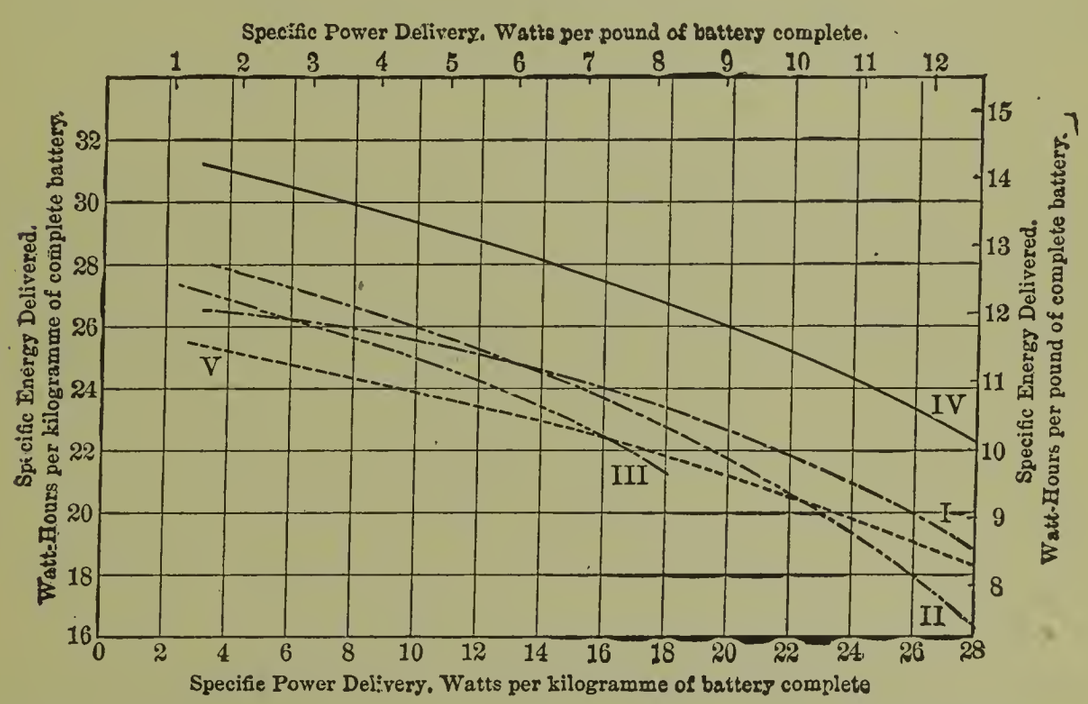


FIG. 7.—CURVES SHOWING USEFUL ENERGY DELIVERED IN DISCHARGING TO A P.D. OF 0.75 VOLT AT VARYING POWER-RATES OF DELIVERY.

All of the tests show that the cells are remarkably immune from deleterious effects due to careless treatment. Cells have been allowed to dry out, have been permanently short-circuited or even charged in the wrong direction. These cells have shown a full restoration of their capacity after a prolonged restoring normal charge.

Conclusions.

The Edison nickel-steel alkaline storage cell, in its large output at heavy discharge rates, its low depreciation in capacity and its durability under severe and adverse treatment, approaches the capabilities of a piece of mechanical apparatus more nearly than is ordinarily credited to electrolytic structures. For this reason it is specially adapted to automobile service, where the treatment is abnormally arduous and severe.

The authors desire to express their indebtedness to Mr. Edison for the cells which he placed at their disposal for test as well as facilities for becoming acquainted with the facts concerning their manufacture. Also to his assistant, Mr. R. A. Fliess, of the Edison Storage Battery Company, who very kindly placed an invaluable collection of experimental data at our disposition. We are also indebted to Mr. C. L. Edgar, president of the Boston Edison Illuminating Company, for the use of his battery in tests and information concerning the same from his assistants.

Discussion.

Prof. C. F. Burgess: I should like to refer to some of the tests which Messrs. Almond and Davidson, in the department of applied electrochemistry of the University of Wisconsin, have carried out on the Edison cell during the past year. Their results corroborate, to a considerable extent, the figures given in the paper just presented. The tests were made on two type "E-27" cells taken from an automobile in service in Madison, and submitted to 20 charges and discharges. The charging rate was 6 hours, and the rate of discharge varied in different runs from 1 to 6 hours. In no case was a watt-hour efficiency obtained which materially exceeded 50 per cent, even on the lower rates of charge and discharge. It seems possible, however, to obtain a slightly higher efficiency, by decreasing the amount of charge given to the battery.

Tests were made on the loss of charge while standing on open circuit, and it was found that standing fully charged during 30 days and then discharged at a five-hour rate, the loss of ampere-hours was 25, or 19.5 per cent. In regard to gas evolution, some interesting observations were made. The total volume of gas on the charge and discharge was measured on several runs. It was found that with a 22-ampere charging rate there was .59 of a cubic foot of gas liberated during the charge, as measured by an ordinary gas meter. At a 35-ampere charging rate the amount of gas liberated was .63 of a cubic foot, while at the rate of 175 armatures—a very high rate—the total amount of gas liberated was 1.59 cubic feet, thus showing where a good deal of the energy goes. It was found that during discharge at a low rate there was about .01 of a foot of gas liberated, and at the highest rates of discharge gas was not liber-

ated in sufficient quantities to be measured. I would like to ask the authors of the paper if they made any observations upon the amount of gas liberated during the charge or discharge of the cell as confirming the above mentioned measurements?

Dr. A. E. KENNELLY: We made no measurements of the amount of gas liberated in the cells.

The gist of our paper is that the Edison cell appears to possess a definite energy-storage capacity per unit weight (in the measurements detailed in our paper about 32 watt-hours per kilo), of which any desired portion may be delivered to the external circuit by suitably proportioning the external resistance, or, in other words, by assigning the electrical efficiency of discharge. Expressing the same result in another way, the energy delivered to the entire discharging circuit (both internal and external) seems to be practically the same within all working ranges, and the externally delivered energy only varies as the external resistance forms a larger or smaller portion of the total resistance in the circuit. The externally delivered energy will be 60, 75, or 90 per cent of the total charge according as the external resistance is 60, 75, or 90 per cent of the total resistance in the discharging circuit, at least to a first approximation sufficient for most practical purposes.

This nearly constant release of energy into the discharging circuit and the hardihood of the cell under severe usage are, perhaps, the most salient points in the cell's behavior.

Mr. S. S. SADTLER: I would like to ask Messrs. Kennelly and Whiting whether they noticed any trouble due to the alkaline solution taking up the carbonic acid from the air. I should think there would be a loss of efficiency in that way.

Mr. S. E. WHITING: Owing to the construction of the cell, which is virtually sealed hermetically, the carbonic acid of the air has very little opportunity to enter the cell.

The Chairman then invited Dr. J. W. Richards to read his paper.

ELECTROLYTIC CONDUCTION.

BY PROF. JOSEPH W. RICHARDS, *Lehigh University.*

Faraday divided conductors into two classes, calling them conductors of the first and of the second classes. The first class conducted the electric current without chemical decomposition, their conductibility decreased with increasing temperature and *vice versa;* they showed no back e.m.f. when the current was stopped. The second class were decomposed when the current passed, that is, the products of their decomposition appeared at the terminals, on passing the current, their conductibility increased with increasing temperature and *vice versa,* and they showed a back e.m.f. when the current was stopped.

Later, Ohm showed that for conductors of Faraday's first class $R = \frac{E}{I}$ and that R is a function of the length and cross-section of the conductor. The specific resistance, i. e., the resistance in ohms of a centimeter cube, is a natural property of the conductor, comparable with its specific gravity or any other physical property. These principles discovered by Ohm are so firmly fixed with regard to conductors of the first class that we will assume their truth in our further discussion.

Later it was shown by Thomson that Ohm's law also applies to conductors of Faraday's second class, if from the applied e.m.f. there be first substracted the e.m.f. corresponding to the work of chemical decomposition which was being accomplished by the current. If E be the total applied e.m.f. and E^1 be the e.m.f. corresponding to the work of chemical decomposition, then $R = \frac{E - E^1}{I^1}$ and R is also here found to be, in this way, a function of the length and cross-section of the conductor. If the terminals be so chosen that the electrolyte is exactly reconstituted by the use of a soluble anode of the same nature as the cathion which is being deposited, then the algebraic sum of the chemical work being performed is zero, and, E^1 being zero, $R = \frac{E}{I}$ which permits of a

very simple and accurate verification of Ohm's law for this class of conductors.

It is admitted then that conductors of Faraday's second class, viz., electrolytic conductors, possess specific conductivity and interpose specific resistance to the passage of the current which is in all respects similar to conductors of the first class. The only difference is that conductors of the second class are decomposed by the current passing through them, and, therefore, absorb an additional e.m.f. corresponding to the chemical potential of the chemical decomposition performed.

Much discussion has been raised regarding the mechanism of the conduction of electricity through these two kinds of conductors. Since no one knows how electricity is conducted through metals, or conductors of the first class, the discussion has been very one-sided, being principally confined to the elaboration of a theory of electrolysis applicable only to conductors of the second class; a theory which links together as one phenomenon the conduction of electricity through the body of an electrolyte and the resulting decomposition produced at the electrodes. According to this theory, the electrolyte is divided throughout as soon as it begins to transmit current into two oppositely charged constituents which take up their march toward the opposite electrodes. Modern electro-chemistry has determined with great industriousness what these charged ions are in a great many electrolytes, what their relative and even their actual velocities are through the electrolyte at different temperatures, and explains the appearance of products of decomposition at the electrodes by postulating the discharge of these charged ions as soon as their migration brings them into actual contact with the electrodes.

If this view is correct, then electrolytic conduction is *per se,* in the body of the electrolyte, different in nature or kind from metallic conduction, in which we know that there is no migration of ions or carrying of the current by the convective action of charged ions.

The object of this paper is to present the thesis that, as far as the conduction of electricity through the body of the conductor is concerned, there is, as far as we can determine, complete identity between metallic conductors and so-called electrolytic conductors.

Marvin has shown[1] that when a current is induced in a circular electrolytic conductor, it behaves toward induced currents in exactly the same manner as a metallic conductor of the same re-

1. *Trans.* Am. Electrochemical Society, III (1903), p. 354.

sistance. In other words, it acts as a conductor, plain and simple, and nothing associated with the experiments show in any way any deviation from the ordinary properties of a metallic conductor.

In the experiments of Richards and Landis[2] on the electrolysis of sulphuric acid solutions, such were shown to act toward feeble direct currents merely as conductors of Faraday's first class, as long as the currents used were so small that the products of decomposition were entirely recombined by the gases present dissolved in the electrolyte. In other words, to understand the phenomena presented in these experiments, the best starting point is to postulate first that the electrolyte is a simple conductor, that it conducts current in the ordinary manner which is true of any conductor, and, having this as a foundation, we may then proceed to discuss *separately,* as an entirely distinct phenomenon, the electro-chemical actions taking place where the current leaves or enters the electrolyte.

Many solid chemical compounds are conductors of electricity; in fact, the majority are. They are, in this condition, undoubtedly conductors in the ordinary sense of possessing metallic conductivity. I have found no scientist who ascribes a different kind of conductivity or a different mechanism of conduction to a solid copper bar from a liquid column of mercury. In fact, liquid mercury is used as the standard of resistance of metallic conductors. There is no sharp change in electrical conductivity when a metal melts, which again points to the identity of metallic conduction through solid or liquid metals. Similarly, there is no sharp change in conductivity when a solid conducting salt melts; it becomes a liquid conductor at the melting point without change in conductivity, just as metals do. The conclusion is that there is conductivity of the same nature in a fluid salt as in a solid salt, and as in a metal, viz., metallic conduction.

The proof of these statements may be found in any text-book of electro-chemistry, such as Ostwald's "*Lehrbuch,*" Vol. II (2d ed.) p. 716.

Since a solid salt conducts metallically, and a fused salt electrolytically, that is, with accompanying electrolysis, we must, in admitting that the mechanism of the conduction through the body of an electrolyte is mere metallic conduction and nothing else, admit also, that the electrolysis is a thing apart from the mechanism of the conduction. The electrolytic or electro-chemical phenomena

2. *Trans.* Am. Electrochemical Society, III, p. 115, and IV, p. 111 (1903).

accompanying the passage of the current are matters occurring only at the electrodes, and have no rational connection with the mechanism of the transmission of the current through the body of the electrolyte.

Much light is thrown upon this subject by the following experiment: A narrow glass tube about 12 ins. long is turned up at the ends, so as to leave about 6 ins. straight tube in the middle. It is warmed, and melted zinc chloride (M. P. 262 deg. C.) poured into it. A Bunsen burner is kept under the middle, to keep it melted, and two zinc rods are plunged into the melted salt in the upturned ends, where the salt at once sets. The cell is now constituted as follows: Zinc — Solid $ZnCl_2$ — Melted $ZnCl_2$ — Solid $ZnCl_2$ — Zinc. Asbestos screens are slipped over the tube so as to define sharply the boundary line between solid and fused salt.

When the temperature is steady for some time, a thermopile is connected with the terminals, a delicate galvanometer reading to microamperes being put into the circuit. The following facts were established: (1) For e.m.f.s up to 3.5 volts, the current passing is proportional to the applied e.m.f. (2) On removing the impressed voltage, there is no trace of back e.m.f., in any case. (3) On continuing a current of 50 to 100 microamperes 15 minutes, there is no trace of electrolysis, either by the formation of gas or metallic deposit or "metallische Schliere" at the junction of the liquid and the solid electrolyte or at the metallic terminals.

The experiment proves to the writer, taking it in connection with the preceding observations, that the liquid salt acts merely as a simple conductor of the same nature as metallic conductors, and by a similar mechanism, and that the question as to whether electrolysis or electro-chemical action takes place is a matter entirely independent of the mechanism of electric conduction through the body of the electrolyte. At any rate, the passage of electric current from solid zinc to solid zinc chloride, or *vice versa,* or from solid zinc chloride to fused zinc chloride, or *vice versa,* is not one of the conditions which produce electro-chemical decomposition of the zinc chloride.

What, then, is electrolysis, and where is its seat? It is electro-chemical decomposition produced at the points where the electric current passes from a fluid compound conductor to a fluid or solid simple-conducting body or to a solid compound-conducting body, and its seat is the contact surface. Its nature or cause is entirely independent of the manner in which the electricity has

been propagated through the body of the electrolyte, and is a function only of the transfer of electricity from the fluid compound to the terminal.

This transfer of energy is accompanied by an unloosening of chemical affinities, and while one constituent of the electrolyte is liberated, the other is potentially freed. This potentially free constituent sets up through the body of the whole electrolyte a condition of chemical stress or stress of chemical affinity, which is transmitted from molecule to molecule to the other electrode, where the complimentary constituent is potentially free. This chemical stress, exhausting itself in diffusion effects, and the primary cause of the migration phenomena, is chemical in its nature and not electrical, and is *caused* by the transfer of the electrical energy at the surface of the electrodes. The migration phenomena are, in this view, secondary chemical effects of the transfer of the current energy at the surface of the electrodes, and are not, in any way, phenomena inseparably connected with the mechanism of the transfer of electric current through the body of the electrolyte.

If this view be accepted, and the writer believes it to be the correct view of the subject, then many phenomena accompanying electrolysis receive their solution. It must be understood that, in this view, the electro-chemical action is regarded as inseparable from the transfer of electric energy from a fluid compound traversed by the current to a solid or liquid conductor of chemically different nature, and, therefore, the generation of the chemical stress and the consequent phenomena of migration are inevitable consequences of the passing of the current. Viscosity by hindering the transmission of the chemical stress hinders the transfer at the electrodes, which can only proceed as the chemical stress is neutralized or exhausted by the motion of the ingredients of the electrolyte toward the two terminals.

It will undoubtedly be at once objected that the writer's view is simply that of current theories, calling electric potential stress chemical stress. Practically, the latter is to be regarded as produced by the former, in the transfer of the current at the electrodes, but the whole point of this discussion is that while electrochemical action is produced directly by the current at the surface of the electrodes, the means of communication between the two electrodes by which the continuance of that action is preserved is in no sense by means of convection currents of charged ions, but is by means of chemical stress transmitted entirely independently of

the mechanism of the conduction of the current through the body of the electrolyte.

The conduction of the current through the body of the electrolyte is simple, normal, physical conduction, a physical phenomena; the transfer of the current from the electrolyte to the surface of the electrodes is physico-chemical, electro-chemical, the point of conversion of electrical into chemical energy and *vice versa*—it is the electro-chemical phenomenon; the reuniting of the constituents liberated at the electrodes, that is, the exchange of parts of molecules so that the compliment of the cathion finally unites by intermediate exchange with the compliment of the anion, is the effect of purely chemical stress exerted upon the electrolyte by the complimentaries of the anion and cathion, and the resulting migration phenomena are caused by, and are the result of, this chemical stress — these are chemical phenomena. The whole of electrolysis is, therefore, comprised in these three consecutive phenomena — first, physical; then physico-chemical or electro-chemical; lastly, chemical.

DISCUSSION.

Mr. CARL HERING: I was interested in the experiment which Professor Richards described, in which he led the current from a solid salt, through a liquid and into a solid salt again; to see where the decomposition would take place, as it is an experiment I myself suggested a number of years ago, but I did not find the proper salts for carrying it out. I am very much disappointed, however, that Dr. Richards used such feeble currents as 100 microamperes, for, in my opinion, the experiment has but little value, because the amount of gas could be readily absorbed by the liquid, or be practically invisible. I am sorry he did not make the experiments with good-sized currents—10 amperes, if necessary—so that the evolution of the gas would be very decided. In that way we could find out in what part of that experiment metallic conduction ceased and electrolytic began, and *vice versa*.

Dr. E. F. ROEBER: From experiments made by Professor Lorenz in Zurich, one would expect that even if Doctor Richards had continued his experiment for a longer time with the same current, the conduction would still have been apparently metallic. Lorenz shows that if the current-density is below a certain value, the metal deposited cathodically has sufficient time to go into solution in "mist" form. This mist passes to the anode and recombines with the chlorine; you have thus perfect depolarization. On the whole you do not get any effect, although you have electrolytic action. Thus the conduction is apparently metallic, although in part it is electrolytic, i. e., follows Faraday's law.

MR. HERING: Where is the surface of the electrode? Is it the surface of the metallic rod, or the place where the solid chloride stops and the liquid chloride begins? In other words, is the solid chloride decomposed or not?

Dr. E. F. Roeber: Professor Lorenz's experiments do not give any answer to this question since he used carbon electrodes directly in the fused bath. Personally, I would expect electrolytic action at the boundary surface of the metallic zinc rod and the solid chloride. In other words, it would be surprising if the solid chloride would not conduct the current in essentially the same way as the fused chloride, although in solid state it may have, of course, an enormously smaller electric conductivity. But, of course, this question must be decided by experiments.

Dr. H. E. Patten: With regard to Prof. J. W. Richards' first point on page 4, he states that for e.m.fs. up to 3.5 volts the current passing is proportional to the applied e.m.f. For non-corrodible electrodes this would mean simply that at low *current-density* the dissolved gases or other ingredients of the electrolyte successfully remove, or depolarize, the products of electrolysis. With no polarization, naturally he would get a straight *CR* line. For his especial case, $Zn - ZnCl_2$ (solid) — $ZnCl_2$ (fused) — $ZnCl_2$ (solid) — Zn, a straight *CR* line means only that in fused zinc chloride, Ohm's law holds good. No polarization is to be expected here with zinc opposing zinc, consequently Professor Richards' second point on page 4 lends no weight to his contention. As to point 3, page 4, the current, some 0.09 coulomb, would deposit about 0.00003 gr. of zinc. This distributed over the electrode, whose size is not stated, would be hard to detect, especially as no mention is made of microscopic examination. The quantity of chlorine to be given off for this current would measure about 0.01 cubic cm and as distributed about the zinc anode would be difficult to detect by the unaided eye, especially through the coating of solid zinc chloride which surrounds this anode. With an easily corrodible anode, such as zinc, we would have certainly most, and probably all the chlorine fixed to form fresh zinc chloride.

On page 6, the conduction of the current through the body of the electrolyte is stated to be simple normal physical conduction, a physical phenomenon. Inasmuch as the other sections are discussing that very thing, as to what constitutes conduction in solids, it can not be termed "simple," although it may be termed "physical." The point is, it is hardly scientific for us to say that part of a process is physical, and leave it at that, while we explain the other part. It is for electrochemists to deal with conduction and electrolysis as a whole.

The experiments of Hittorf are interesting in this connection. He found on electrolyzing fused silver sulphide and then allowing it to cool, that metallic threads ran through the mass.

Dr. W. D. Bancroft: In this paper it is stated that many solid chemical compounds are undoubtedly metallic conductors. That would seem to be purely an assumption. Doctor Richards tries to prove it by saying that because a solid and a liquid metal conduct metallically, therefore solid salt is a metallic conductor. I do not see why he did not put it around the other way and say that because solid and liquid silver iodide conduct electrolytically,[1] then copper does. On the next page he says that "Since a solid salt conducts metallically" and then goes ahead. If you reject his assumption, there is nothing left of the

[1]Cf. Lehmann. Molekularphysik, 225.

basis of his theory. I quite agree with Mr. Hering and Mr. Patten as to the utter worthlessness of the experiment in its present form. When it comes to detecting a loss or gain of 0.03 mg zinc on the zinc rod electrodes by the eye, it is asking a good deal of us to accept that. Another point is of historical importance only. Doctor Richards says that it was shown by Thomson that Ohm's law also applies to electrolytic conductors if the counter electromotive of polarization be subtracted. Since both Wheatstone and Daniell were quite clear on this point, the reference to Thomson is unfortunate.

Prof. L. KAHLENBERG: I desire to call attention to the fact that the idea that the changes of concentration of the electrolyte at the electrodes as the electrolysis proceeds is due to chemical stress or strain is not at all new. In a paper which C. J. Reed presented to the Franklin Institute a few years ago, he stated that if the products of electrolysis could be taken from the electrolyte at the electrodes without the aid of the electric current, the usual concentration changes at the electrodes would take place just as in electrolysis. Thus the deposition of zinc at the cathode would deplete the solution in zinc at that point, and consequently zinc would pass over to that place by diffusion. This view has also been held by others from time to time, and I have alluded to it in a paper on "Electrochemical Theories" which I presented to the American Electrochemical Society at its initial meeting. I quite agree with those who have spoken as to the worthlessness of the experiments described as showing that we have here a case of metallic conduction.

Prof. J. W. RICHARDS: In regard to the minuteness of the products and of the currents which I used, I will say that I very frequently use smaller currents than were used here, and the evolution of hydrogen and oxygen caused by these currents is very easy to observe; so that if there had been a trace of chlorine I am sure it would have been noticed, because of my experience with the use of currents of this kind. I can not speak with positiveness as to whether the zinc cloud produced by that current could have been seen, but I have seen it with very small currents. In regard to the use of 3½ volts, I will say that that was all the voltage I had at command at the time, and that to have caused a current of 10 amperes, as Mr. Hering suggests, would have required something like 3500 volts, and such large currents are not always available. As Mr. Patten and Mr. Bancroft have remarked, and the idea is one which I wish to impress on the Society, others have been thinking of the practical identity of the two kinds of conduction. I know that Professor Thompson and others have been working to show that ordinary metallic conduction is by a convective electronic process. The whole point of the discussion, as I take it, is that the similarity of the two kinds of conduction has been suspected, and perhaps verified, not only by this experiment, but by a number of other considerations.

The Chairman then requested Doctor Roeber to present Prof. Dr. Richard Lorenz's paper, in the absence of the author. The paper was read from the MSS. with the illustrations printed and distributed among the members.

ON THE ELECTROLYSIS OF FUSED SALTS.

BY PROF. DR. RICHARD LORENZ, *Polytechnicum, Zurich, Switzerland.*

The scientific production and the industrial utilization of the products of the electrolysis of fused salts have, during the last two decades, been greatly enhanced, partly owing to the enormous progress, which raised electrometallurgical processes to an importance at first hardly suspected, and partly owing to the researches which have been conducted with the object of studying the theory of the electrolysis of fused salts.

Pursuing the latter aim the Electrochemical Laboratory at Zurich has for some years past published a large number of researches upon the subject of the electrolysis of fused salts. The author of this paper has, in co-operation with his students, studied the phenomena accompanying the electrolysis of fused salts qualitatively as well as quantitatively both with regard to the qualitative treatment of the substances to be electrolyzed, and the determination of the amount of polarization, the e.m.f. of the current-generating fused systems, the conductivity, the voltage of decomposition, and particularly the application of Faraday's law. Based on the collection of data of facts, it was also possible to determine the outlines of a theory of the electrolysis of fused salts up to temperatures of about 1000 deg. C., and to deduce from them the consequences of the same as regards the limitations of Faraday's law, and as regards prospective technical processes.

The choice of a suitable apparatus is a constant difficulty recurring in new forms when solving electrolytic problems of fused salts. A characteristic example of this is the electrolysis of fused zinc chloride. If for instance one tries to fuse this salt in a porcelain crucible heated in a free Bunsen flame, and to electrolyze it between two carbon electrodes, no matter in what direction they project into the salt, no normal electrolysis of zinc chloride will take place. A strong evolution of gas immediately takes place, and the electrolyte shows an exceptionally high specific resistance. The contents of the crucible foams and overflows after a short time, and

zinc will not be found deposited at the bottom of the crucible, nor on the cathode, while the electrolyte itself has become strongly basic after the electrolysis. Variations of the conditions of the experiment remain fruitless. If one asks for the reason for the failure of the experiment it is to be ascribed solely to the incompleteness of the apparatus used, to which, in the case of chloride of zinc, must be added the exceptional hygroscopic quality of this salt.

It was thus very natural that the main interest of the author at the beginning of his studies should be turned toward the construction of various apparatus. An apparatus of very general application is the wrought-iron furnace intended for the V-shaped electrolyzer, which H. Helfenstein described in detail (*Zeit. Anorg. Ch.*, Vol. 23, p. 260, Fig. 2, 1900). The requirements of every such apparatus are that it be easy to operate at the best attainable constancy of temperature. The great extent to which the latter condition especially influences and determines the phenomena and results of the electrolysis of fused salts will be the subject of various explanations below. With the introduction of the V-shaped receptacle the question as to the suitable form of the electrolyzer for laboratory research was solved in a relatively simple way. Up to 700 deg. C., V-tubes of hard glass are used, above this temperature they are of porcelain. The other type to be considered is the cylindrical receptacle, whose simplest form is probably represented by the common porcelain crucible. The differences between these are of great importance for the explanation of the theory of the electrolysis of fused salts, and will be considered more in detail below.

Another question of importance, mainly in connection with the question of the current efficiency, is the way in which the electrolyte is treated beforehand. In this respect it is especially the hygroscopic haloid salts which necessitate such a preparation; among these is to be recalled more especially Bunsen's method of melting together the haloid salts of the heavy metals with the alkaline haloids, in order to be able to electrolyze them; in this way he produced low melting mixtures, which thus rendered the desired results. This method of Bunsen has been repeatedly applied and varied by other experimenters in their scientific researches, as also on the industry; and for a long time this method, which up to a certain degree is reliable, was applied to improve the current efficiency. The researches of the Electrochemical Laboratory of Zurich have for the first time shown that Bunsen's solution of the problem in some cases may be improved upon by a method never

before used, consisting of preparing the electrolyte in advance by means of water-absorbing gases. Of this process a complete description will also be given below.

The author has, partly together with his students, constructed several furnaces for laboratory use (*Zeit. f. Electrochemie,* Vol. 7, pp. 278, 279, 1900), and has published several methods of research intended for pyroelectric measurements (*Zeit. Anorg. Chem.,* Vol. 19, p. 221, 1899; Vol. 20, p. 335, 1899; Vol. 21, p. 311, 1899; Vol. 25, p. 140, 1900; Vol. 27, p. 159, 1901; Vol. 28, p. 388, 1901). In what follows there will be given some prominent examples of important phenomena and also quantitative results of the electrolysis of fused salts.

Some Prominent Qualitative Phenomena in the Electrolysis of Fused Salts.

Phenomena which are apparently abnormal are by no means rare in the electrolysis of fused salts, even to an extent that it can, on the contrary, be considered exceptional only when the electrolysis takes place according to Faraday's law. To illustrate this assertion, which is here made in a broad and general way, let us consider the electrolysis of chloride of lead, a case which even Faraday had studied. (*Phil. Trans.,* London, 1834; *Pogg. Ann. d. Phys.,* Vol. 33, p. 481, 1834; *Ostwald Klass.,* No. 86, pp. 42, 44, 65, 90, 92; No. 87, pp. 78, 86, 119, 148), and which he used for the proof of the law named after him. He succeeded in proving the validity of his law when applied to fused salts also, only by using a device which, in view of the conditions of those days, must be considered ingenious. Faraday used for the cathode melted lead, into which metal the carbon electrode was dipped. He thus avoided all those accompanying interfering phenomena and the influences tending to lower the current efficiency, which are to be mentioned later on.

When fused chloride of lead is electrolyzed, for instance, in a V-tube, it is not a matter of indifference whether a salt is utilized which has already been used in electrolysis, or whether entirely new chloride of lead is employed. In the former case one will always obtain by quantitative measurements more constant values than with fresh chloride of lead. The explanation of this fact will be given below. When the electrolysis has been carried

on for a sufficient length of time between carbon electrodes at temperatures between 600 and 700 deg. C., the cathode space has a dark color, while the anode space is yellow and clear, especially where the chlorine is developed. A black mist (Schliere) forms over the deposited lead regulus toward the anode, which mist is again destroyed by the chlorine. This mist does not consist of mechanically-loosened particles of carbon, but is a real *metallic mist* or *fog*. If the salt is heated to a higher or lower temperature, the anode space as well as that of the cathode will become a yellow-red; a layer of blask mist will then still appear, but only directly above the regulus. By using a high-current density in the electrolysis, continuous-glow phenomena appear at the anode, which are particularly troublesome in measuring the polarization and other values. The current then suddenly sinks to zero, the voltage between the terminals increases, and the carbon electrode begins to glow intensely. A sort of spark discharge takes place over the whole surface of the carbon anode submerged in the fused electrolyte, and it has the appearance as though the anode surface was going to be lifted off the rest of the electrolyte by means of an opaque gaseous stratum. A sound accompanies this phenomenon resembling that of an induction apparatus of law power. A mechanical shaking of the anode is sometimes sufficient to cause this glowing at the anode to disappear, while sometimes it disappears by itself. This phenomenon of the glowing of the anode was first observed by R. Lorenz (*Zeit. Anorg. Chem.*, Vol. 10, p. 78, 1895), later by Minet, when he electrolyzed fused aluminum chloride; by Hulin in electrolyzing a fused mixture of sodium chloride and lead chloride (*Zeit. f. Angew. Chem.*, 1897, p. 494); also by Gross (*Electrochem. Zeit.*, Vol. 4, p. 1; *Zeit. f. Electrochem.*, Vol. 3, p. 486, 1897); and by Alexander in the electrolysis of a mixture of silver chloride and silver sulphide (*Zeit. f. Electrochem.*, Vol. 5, p. 93, 1898). This phenomenon was observed in the electrochemical laboratory of Zurich by V. Czepinski (*Zeit. Anorg. Chem.*, Vol. 19, p. 245, 1899). He could observe the same phenomenon very frequently in the electrolysis of fused cadmium chloride, but only rarely in the electrolysis of the bromides of lead and silver. A fully satisfactory explanation of this phenomenon does not exist. It is always referred back to a transition resistance, caused by a layer of vapor around the anode, so that, at this electrode, the phenomenon of the Wehnelt interruptor takes place.

Let us return to the above-mentioned phenomenon of the metallic mist, the nature of which is not clear without further elucidation. It might be a case: 1), Of a real solution of the metal in its fused haloid salts; or 2), of a mere pulverization of it in suspension. In the latter case the metal would be mechanically suspended in the melted mass in the form of an extremely fine mist. This phenomenon is dependent to a high degree on the temperature and the vapor tension of the metal, respectively. With the more volatile metals it occurs at a lower temperature than with those that are volatized with more difficulty. The extension of the colored mass in the fused bath is also dependent on the temperature, so that the appearance is quite like that of diffusion. It is clear that such a phenomenon must have a most important influence on the current efficiency; and this applies to all the haloid salts of heavy and the light metals, when electrolyzed in the fused state.

The author has, in co-operation with A. Helfenstein, studied these relations quantitatively for an entire series of fused salts (*Zeit. Anorg. Chem.*, Vol. 23, p. 255, 1900). The chief results of these researches will be set forth below. The phenomenon of the mist can be produced more or less distinctly according to the temperature; at higher temperatures these mists appear and fill the melted masses more and more; at lower temperatures they condense, sink to the bottom, and the bath becomes clearer. The metallic mist which is thus produced has for most metals a very characteristic color; the zinc mist is colored a silver-white, the cadmium mist is fawn-colored, the lead mist brown-black, the silver mist completely black. The author has, together with G. Auerbach, made experiments (*Zeit. Anorg. Chem.*, Vol. 28, p. 41, 1901), which makes plausible the assumption that a real solution of metals in fused salts may exist. This solubility of the metals in the fused baths may, perhaps, have some connection with a second phenomenon, which often follows in joint action with light rays and is especially noticeable with the iodides. It can be expressed by the following equation:

$$\overset{\text{II}}{n\,M\,I_2} = (n-1)\,M\,I_2 + \underset{\text{metallic solution}}{M} + I_2.$$

Traces of the halogen accordingly escape without the influence of the oxygen or the humidity of the air, and there remains a saturated

solution of the metal in the fused bath. In a paper read before the Seventh General Meeting of the German Electrochemical Society (*Zeit. f. Electrochemie,* Vol. 7, p. 281, 1900), the author referred to the similarity between the relations existing here and the formation of the latent picture of a photographic plate. The phenomenon of the metallic mist has been made the subject of subsequent researches, and in a recently-published paper by S. Gruenauer (*Zeit. Anorg. Chem.,* Vol. 39, p. 389, 1904) the same was even photographically recorded under particularly favorable conditions of the experiment. By means of a strong sidelight one clearly discerns the innumerable fine and minute drops of which the phenomenon of the mist is composed.

The formation of the metallic mist in the fused baths has been observed repeatedly in practice. See, for instance, F. Haber's report on the formation of metallic mists in the Hall aluminum process (*Zeit. f. Electrochemie,* Vol. 9, p. 361, 1903), but they have frequently been connected with the formation of a subchloride, or have even been confounded entirely with it. For the reguline deposit of metals from fused salt, the phenomenon of the metallic mist is very important, because such a deposit results only when the saturation of the fused bath with the metal is reached, or nearly so. In the deposition of metals the fused masses act as *depolarizers* on the cathode, which has as the further consequence that the solution pressure of the reguline metal cannot be reached during the first phases of the electrolysis, nor by using very low-current densities. When the metallic solutions and the metallic mist reach the sphere of the anode, they themselves will again act as *depolarizers* upon the halogen deposited there, as they prevent the formation of free halogens. This doubly-acting depolarizing force can rise to very high values. This may also be expressed scientifically in the following way: An electrolytic cell filled with a melted salt, in the electrolyte of which diffusion and thermal eddy currents can take place freely from the cathode to the anode, represents an electrolytic system of exceptionally high "residual current" ("Reststrom") capacity. The residual current, that is, the current whose direction is opposed to the polarization, originates from the metallic mist formed at the cathode, wandering toward the anode, where with the deposited anions it regenerates the original product by chemical reunion. The rapidity (intensity?) of this residual current depends upon the rapidity of the movement of the metallic mist through the

electrolyte, on the rapidity of the reformation of the metallic mist at the cathode, and on the rapidity of the recombination with the deposited anion. But the rapidity of the deposition of the cathions and anions is determined by the current strength used in the electrolysis. When this current strength is great, the rapidity of the deposition will exceed the rapidity of the residual current and a practical result of the electrolysis is obtained. When, on the other hand, the current strength is small, the residual current phenomenon may predominate to such a degree that a result of the electrolysis cannot be noticed. Then will arise the phenomenon of a pseudo-metallic conduction of electricity in the fused salts. These few paragraphs, which are the results of our researches extending over years, form the basis for the understanding of the electrolysis of fused salts.

Another series of phenomena present themselves to us when we consider, for instance, the electrolysis of fused chloride of zinc. There are two kinds of zinc chloride on the market, the one yielding good, the other poor, results, when electrolyzed; their empirical differences were established by R. Lorenz (*Zeit. Anorg. Chem.*, Vol. 10, p. 78, 1895), and later on by R. Lorenz in co-operation with H. S. Schultze (*Zeit. Anorg. Chem.*, Vol. 20, p. 323, 1899). By the aid of the researches of S. Gruenauer (*Zeit. Anorg. Chem.*, Vol. 39, p. 389, 1904), the author succeeded in clearly explaining the apparently very complicated relations of the electrolysis of fused chloride of zinc. The electrolysis of the above-mentioned two kinds of zinc chloride differ greatly from each other. The kind of zinc chloride which is easy to electrolyze yields gas from the moment of the turning on of the current at the anode, as well as at the cathode, without giving rise to a turbidity of the electrolyte, which will be described below. Hydrochloric acid alone escapes at the beginning of the electrolysis, while chlorine appears only gradually. The deposition of zinc begins at once on closing the current, but it was shown that the deposited zinc is dissolved at once after its deposition in the strongly acid electrolyte, consequently, as a rule, the amount of deposited zinc varies considerably at the beginning of the electrolysis. By the time the deposition of zinc becomes regular, the strong evolution of chlorine has already begun, and the electrolysis from now on proceeds "normally." Such a normal electrolysis is, however, not observed with the kind of zinc chloride which does not electrolyze well. With this kind the electrolyte, even

after only a few minutes, appears filled with an opaque mass. Hydrogen is also developed at the cathode in this case, the deposition of zinc begins immediately on closing the circuit, and at the anode chlorine is at once developed, instead of hydrochloric acid, as with the kind which yields good results. The intense cracking at the anode on closing the circuit is quite striking. It always occurs during the electrolysis of fused basic electrolytes, and is due to the pulverization of the carbons. This noise, however, ceases before the cathodic evolution of gas, and it is entirely absent in the presence of quantities of water. The anodic carbon electrodes are rapidly attacked and flow down in the form of a brown substance. Blue clouds rise at the cathode making the electrolyte impure; the electrolyte simultaneously becomes opaque by the precipitation of $Zn(OH)_2$. This substance is shown to be zinc dust formed through a pyrochemical process in a fused bath. The current can be sent for hours through such an electrolyte which has thus been made impure by zinc dust, without making it transparent. The electrolyte has a blue-gray color, until finally the turbidity begins to settle again. The carbon cathode mostly shows a tree-like outgrowth of a grey appearance, the zinc regulus itself is quite covered with the deposited substance. This deposited substance is, as mentioned before, zinc dust, a mixture of zinc oxide or zinc hydroxide with finely-powdered zinc. It is due to the fact that zinc oxide is set free by the electrolysis of an electrolyte of zinc chloride containing water, and the metal mist of zinc is condensed on it by surface action.

The kinds of zinc chloride of commerce, which may be electrolyzed with good results, contain salammoniac, while the other kinds are free from all impurities. The latter may be changed into the former by first evaporating it to dryness with a concentrated aqueous solution of hydrochloric acid, stirring constantly, and then melting it in a porcelain crucible. How, then, may the problem be solved to effectuate a normal electrolysis of quite pure fused zinc chloride, when the kind containing salammoniac is the only one yielding good results? Lorenz and Gruenauer investigated this problem, first by making up different mixtures of chloride of zinc and salammoniac and finding the results obtained by their electrolysis. It was thereby discovered that the power of the salammoniac to give off its moisture is only an incomplete one, and is also so dependent on adhering to certain definite conditions in the preparation of the electrolyte, that for this reason alone the addition of

salammoniac cannot be considered a good means for bettering the conditions of the electrolysis of fused chloride of zinc. Instead of water one has salammoniac in the bath, which has to be removed electrolytically, as set forth above, before normal electrolysis takes place. It escapes in the form of hydrochloric acid and nitrogen. The disturbing phenomena which appear in the electrolysis of fused zinc chloride depend on the fact that the water present in the fused bath brings about hydrolysis, as shown in the following equations:

$$ZnCl_2+2H_2O=Zn(OH)_2+2HCl,$$

$$ZnCl_2+H_2O=Zn\begin{matrix}OH\\Cl\end{matrix}\quad HCl,$$

$$2ZnCl_2+H_2O=Zn_2OCl_2+2HCl,$$

$$(n+1)ZnCl_2+nH_2O=ZnCl_2+nZnO+2nHCl.$$

The last equation expresses the formation of any zinc oxychloride. It is not unimportant for the electrolytic process which of these different hydrolytic separations actually prevails; for this case the above equations may be divided into two classes, namely, one in which the basicity of the bath is determined chiefly by the entrance of atoms of oxygen to the fused mass; the other, in which the basicity originates from OH groups which can be split off as OH ions. Numerous observations during the electrolysis of fused salts have led the author to the opinion that carbon anodes in particular are attacked by OH ions in a different way than by fused baths containing oxygen. The attack of the carbons in fused alkaline hydrates takes place with the formation of mellith acid products, while the discharge of oxygen disintegrates the carbon rod into splinters of carbon during the formation of CO and CO_2. What the character of the hydrolysis is with zinc chloride could not yet be determined. It must, at any rate, go back to the law of mass action when hydrochloric acid is added. This was the point of view from which the above question could be answered. Lorenz and Gruenauer for this reason turned their efforts toward the drying of the zinc chloride by means of hydrochloric acid gas, and thus obtained the actual material $ZnCl_2$ in a convenient state for electrolysis, when *certain specific conditions were observed* (the time of drying; the velocity of the drying gas current passing

through the concentrated solutions of chloride of zinc; the form of the apparatus). The carrying out of these experiments necessitated the construction of a special apparatus, the "dehydratisator." It could be shown that *even less than* 0.78 *per cent of water is sufficient* to make a zinc chloride bath yield poor results by electrolysis. The electrolysis of zinc chloride thus completely freed from water and acid will then proceed normally.

It has been shown by two examples, chloride of lead and chloride of zinc, what surprising phenomena may take place in the electrolysis of fused salts. The one salt, being absolutely free from water, shows by electrolysis in the fused state, the existence of only such interferences as arise through the residual-current phenomenon; the other salt, which is hygroscopic, and from which the last traces of water cannot be removed even by heating for hours at a red heat, is subject to interferences due to basicity of the electrolyte. But even when the causes of the latter are removed by a proper preparation of the salt before it is electrolyzed, the electrolyte thus obtained will nevertheless still be subject to the interferences caused by the residual-current phenomenon. There are thus clearly and distinctly separated from each other two phenomena which occur in manifold combination in the electrolysis of fused salts, and which can be so complicated that it was formerly considered impossible to carry out the electrolytic process with fused salt in a proper way and with a purpose, except by experience gained purely empirically.

On the Application of Faraday's Law in the Electrolysis of Fused Salts.

A quantitative treatment of the electrolysis of fused salts is possible only when the above-mentioned disturbances are carefully taken into consideration. The disturbances which are produced by the basicity of the electrolyte may be avoided if care is taken to make adequate preparation for the fusion. These disturbances, however, which are produced by the residual-current phenomenon and the development of the metallic mist, first had to be subjected to a special investigation in order to determine the precise facts. Hereupon the researches of the author, in conjunction with A. Helfenstein, give information (*Zeit. Anorg. Chem.*, Vol. 23, p. 255, 1900). These may be briefly stated as follows: The residual-current phenomenon, produced by the development

and migration of the metallic mist in the electrolysis of fused salts, has, as a consequence, that the quantities liberated at the electrodes are not developed in conformity with Faraday's law. The current efficiency does not reach 100 per cent, but is less. Now all causes which tend in the direction to make the rapidity of deposition become large with respect to the rapidity of recombination of the deposited ions, due to the residual-current phenomenon, tend to produce an increase in the current efficiency. One of these causes is current strength. If, in a given apparatus, the current strength is steadily increased, then the current efficiency rises at constant temperature.

Numerous numerical demonstrations and curve sheets which were collected by Helfenstein for the electrolysis of quite different fused salts demonstrate the above-mentioned fact. Another cause of this is the form of the apparatus, its dimensions, and the position of the electrodes. When the paths in the apparatus are great, and the breadth is small, the thermic eddies which drive the metallic mist from the cathode to the anode will have a weaker action than when the path from one electrode to the other is short, and when the electrodes face each other with large surfaces. Consequently, the rapidity of recombination will be diminished for a given current and the current will increase. If, for instance, the distance between the electrodes is increased more and more in an experiment in a given V-tube, the current efficiency will increase at constant current strength and constant temperature. A further cause is the temperature. An increase of the temperature increases the formation of the metallic mist, the solubility of the metal in the bath, and also the thermic eddy movements. Consequently, the current efficiency will diminish for a given apparatus and constant current strength with increasing temperature. This occurs very rapidly so that the electrolyte strives toward a condition of pseudo-metallic conduction in such experiments also. These principles appear to me to be extremely important for the rational carrying out of industrial processes with fused salts. They give us clear indications for the construction of apparatus, for the choice of current density, temperature, etc.

But there are also specific causes of the increasing of the formation of metallic mists. One of these is the volatility of the metal. The nearer the metals are heated to their boiling point, the greater is their vapor tension, and the more will they tend to form metallic

mists. If, therefore, we deposit in similar apparatus, at the same constant temperature and with the same current strength, first cadmium and then lead, the current efficiency will be less for the cadmium electrolysis than for the lead electrolysis, because the former metal is heated nearer to its boiling point. Moreover, there are added several other specific losses to those which are determined by the residual current. These are due to the fact that the metallic mist can reach the surface of the bath. There it can be oxidized by the oxygen of the air, or when there is no oxygen the mist diffuses out from the bath and deposits itself on the walls of the vessels as a distillate. The solubility of the metals in the bath is also different, a fact which ought to be considered in quantitative experiments. After these disturbances were studied so carefully, it became possible to avoid them. The most complete avoidance of

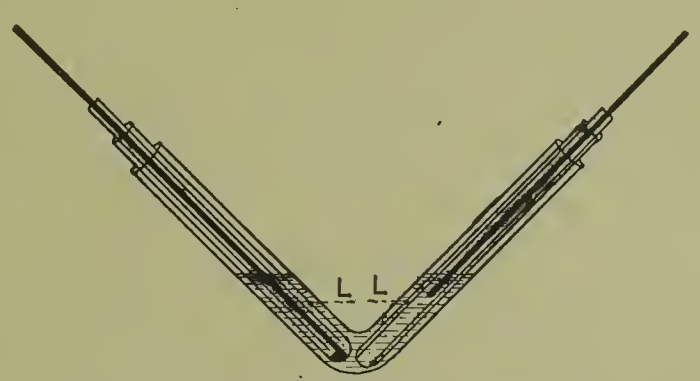


Fig. 1.— Encasing apparatus.

these disturbances would consist in preventing the formation of the metallic mists.

The author, together with Appleberg, made the remarkable observation that there are substances which, when added to the fused bath, almost completely prevent the formation of the metallic mists. Owing to this observation there is opened an entirely new sphere in the theory of such auxiliary additions to the baths, which, as is well known, are so important in the industrial electrolysis of fused salts. Who does not know how important the composition of an aluminum bath is for the current efficiency in this process. Formerly it was believed that these additions served chiefly for the regulation of the fusion point and of the specific gravity of the fused electrolyte. To-day we know that under certain conditions they may be credited with a direct effect on the improvement of the current efficiency. But it is not always possible to accomplish the desired results by additions to the bath.

It remains then only to prevent the diffusion of the metallic mist. The author, together with Helfenstein, found that the nature of the metallic mists is such that they cannot penetrate through diaphragms of clay (Tondiaphragmen). The mists may also be kept together by encasing the surroundings of the electrodes. This is done by the application of the "encasing apparatus" used by Helfenstein.

The arrangement of this apparatus is as follows (see Fig. 1): The carbon cathode is first put into a closely-fitting case of highly-infusible glass, which projects out over the end of the V-tube. At the lower end of this case the carbon projects about 5 mm. The electrode, insulated in this way, is now placed into a highly-infusible test-tube of 13 mm internal diameter, which is provided with a round hole (designated by *L* in the figure) 3 mm in diameter at a distance of 45 mm from the bottom. The purpose of this hole is to establish communication between the space in the V-tube and that around the anode. The test-tube, together with the insulated electrode, is placed in the cathode branch of the V-tube. The hole in the test-tube is turned upward, so that the fused bath can circulate freely. The anode carbon is similarly encased with the exception of a few changes occasioned by the functions of the anode. As the halogen must escape from the bath into the air, a carbon electrode, 2 mm diameter, is first placed into a glass tube 8 mm inner diameter, and this again into a test-tube similar to that for the cathode; the diameter of the latter is about 15 mm. The hole is only 40 mm from the bottom; the inner glass tube, in which the anode lies freely, is broken off at the lower end into two teeth, so that it cannot rest wholly on the bottom of the reagent glass and disturb the communication between the anode and the cathode spaces. The encased anode rests with its case upon the case of the cathode.

In this apparatus Faraday's law is fulfilled under all conditions, so that one now is wholly independent of current strength, temperature, distance between electrodes, and the duration of the electrolysis. In the use of this apparatus the above-cited conditions for the adequate separation of anode and cathode spaces are fulfilled. One will be independent of the variations due to the solubility of the metals in their baths, by previously saturating the bath with the proper metals at the temperature at which the electrolysis takes place.

The diffusion of the metal vapors into the air is avoided by allowing the surface of the bath in the cathode branch to freeze. There will then be obtained almost quantitative current efficiencies, as is shown by the following curve sheet, Fig. 2:

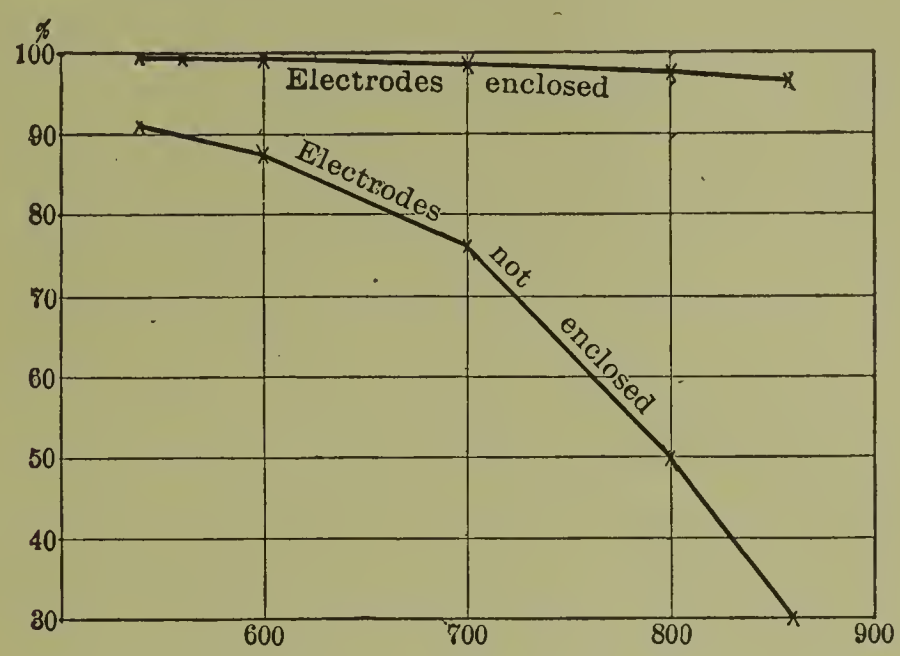


FIG. 2.— EFFECT OF INCLOSING THE ELECTRODES.

The current strength was the same for both curves. The figures which were obtained for the outputs at different temperatures are: 560 deg., 99.5 per cent; 600 deg., 99.3 per cent; 700 deg., 98.5 per cent; 800 deg., 97.8 per cent; 860 deg., 96.8 per cent. By taking into account the errors which still remain in this apparatus (namely, that the metallic mist vaporizes in the cathode space from the surface of the bath into the air and deposits again as metallic lead in the tubes), and adding to the result the losses thus obtained, one will, in fact, obtain the maximum output of 99.98 per cent, whereby the fulfillment of Faraday's law seems to be proved. The only disadvantage found in working with this encased apparatus is that the bath has a high resistance. By the use of clay diaphragms it is possible to avoid even this disadvantage without interfering with the quantitative results. In this case also outputs up to 99 per cent are obtained so that the rest is to be regarded as loss by diffusion to the outside at corresponding temperatures.

After it was thus proved by these researches that Faraday's law is fulfilled in the electrolysis of fused salts when the disturbances which are caused by the residual current are avoided, it was also proved thereby that the figures for the current efficiencies, which are obtained in the electrolysis of fused salts *without avoiding the residual current,* were conditioned only by the residual current, and

that there are no other causes. Now since this residual current, as was shown above, can be clearly defined, the idea suggested itself that it ought to be possible to represent its effect quantitatively. The relations between rapidity of the deposition and that of the recombination had to be like that of some well-defined mechanism. That this is, in fact, the case the author was able to show in co-operation with A. Appelberg (*Zeit. Anorg. Chem.*, Vol. 36, p. 36, 1903). If in a given apparatus the current strength is allowed to fall, the current efficiency falls. Finally, a point will be found where the rapidity of deposition becomes exactly equal to that of recombination. The current efficiency curve, when plotted as a function of the current strength, does not cut the axis of abscissas at the zero point of the system of co-ordinates. We obtain, then, no apparent electrolytic action, even without going to zero with the current strength. These relations have already been mentioned above, but it is of interest that they may be described mathematically by a formula which shows the current efficiency as a function of the current strength. This formula is

$$a = 100 - \frac{k}{i^n}$$

in which n and k represent constants of the apparatus and temperature, a the current efficiency, and i the current strength. This formula agrees so completely with the observations that it suffices to plot two determinations of the current efficiency in an electrolytic trough and base on them the whole series of current efficiencies at different current density which one wishes to use for electrolysis.

The following may serve as an example:

Current strength in amperes.	Observed efficiency.	Calculated efficiency $n = 0.83$.
2	99.7%	99.4%
1	*98.9	98.9
0.5	97.4	98.0
0.1	93.3	92.6
0.05	84.4	86.8
0.03	75.4	79.8
0.01	40.6	49.7
0.005	*9.7	10.6

The observations marked * were used to determine the constants. The constant k is most easily obtained when the cur-

rent efficiency is determined at 1 ampere, for k is nothing else than the loss of output at this current strength.

An interesting apparent exception to the quantitative laws here presented, which apply in general to the electrolysis of fused salts, is the material PbI_2, the electrolysis of which in fused form G. Auerbach has investigated exhaustively (*Zeit. Anorg. Chem.*, Vol. 28, p. 1, 1901). Important variations in the current efficiency take place especially at 700 deg. To explain this, Faraday accepted the theory of the formation of lead tetra iodide. Auerbach's researches, however, brought forth the fact that there is no ground for this; the irregularities appear rather to be originally due exclusively to the physical properties (solubility of the metal, diffusion, etc.), with only this difference, that these disturbances are increased in the case of lead iodide. This may have its origin in the greater solubility of the iodine in the bath, as compared with chlorine, and seems to show that the part taken by the anions in the disturbances in the electrolysis of fused salts has not yet been clearly shown.

It remains now to consider the quantitative relations at the anode in the electrolysis of fused salts. Upon this point Auerbach, in the Electrochemical Laboratory at Zurich, found quantitative proofs. If a fused salt is electrolyzed in a given apparatus, always under the same conditions as to temperature and current strength, one can be sure to invariably get the same current efficiency for the metal within the limits of error. The residual-current phenomenon presents itself so exactly that for certain conditions of experiment there will result a certain loss by recombining. It should be almost self-evident that, as the loss of metal arose through a recombining with the anion, for instance chlorine, the loss at the anode should consequently be exactly as great. But no one had as yet determined the amounts which appear at the anodes in the electrolysis of salts. So when we began our researches we were astonished to see that the current efficiencies in the electrolysis of fused lead chloride were not identical at the cathode and at the anode. But when the electrolysis was continued long enough they became so. It was, therefore, shown that there was a time phenomenon in the current efficiency at the anode.

In the first stages of the electrolysis, the current efficiency at the anode for chlorine is lower than that of the lead at the cathode, and rises gradually up to it. The excess of chlorine loss over the

lead loss is due to the fact that the carbon anode saturates itself only slowly with chlorine. As soon as this saturation of the carbon anode is complete, the efficiency of the chlorine becomes the same as that of the lead. Carbon anodes which have already been used show a more rapid rise in the chlorine efficiency; an equality of the anodic and cathodic efficiencies is, therefore, reached sooner than with new carbon anodes. The process in the electrolysis of fresh chloride of lead with weak currents is consequently understood to be that a part of the separated chlorine is absorbed by the carbon rod at the beginning of the electrolysis, and that a further part which is equivalent to the loss in lead efficiency is regenerated to lead chloride by the metal solution, and only the remainder escapes as free chlorine. An addition of oxide of lead to the chloride of lead during the electrolysis has no effect on the cathodic efficiency, but on the other hand no chlorine is disengaged at the anode and the carbon rod becomes oxidized by the escaping oxygen. Electrolytes containing oxygen pulverize the anode carbon, as has already been mentioned above, while in electrolytes which are free from oxygen the anode carbon is refractory toward chlorine.

In what follows some further information is given on e.m.f's and polarization.

E.M.F's and Polarization in the Electrolysis of Fused Salts.

The counter e.m.f's which arise in the electrolysis of fused salts were determined by R. Lorenz together with V. Czepinski (*Zeit. Anorg. Chem.*, Vol. 19, p. 208, 1899); by O. H. Weber (*Zeit. Anorg. Chem.*, Vol. 21, p. 305, 1899); and by R. Suchy (*Zeit. Anorg. Chem.*, Vol. 27, p. 152, 1901). They measured the polarization by the discharge through a galvanometer of high resistance (method of polarization discharge), but repeatedly controlled the values thus obtained by combination of chains of fused salts. In this way there were determined, among others, chains of the type of the Daniell cell, which will, however, not be further considered here. It was found that the polarization was dependent on the appearance of the metallic mist in quite a similar way as the current efficiency is, and, therefore, also on the form of electrolytic trough used. In an electrolytic trough in which the metallic mist can diffuse from the cathode to the anode, the polarization will be less when an appreciable effect is exercised on the anodic potential as soon as the

metallic mist reaches the anode. The e.m.f. of chains in which the metallic mist reaches the anode appears to be reduced quite considerably in contradistinction to one in which this is not the case. The metallic mists must be considered as powerful depolarizers when they arrive at the anode. This fact could be observed in an experiment with the above-described encasing apparatus (Fig. 1). As was mentioned, the anode and cathode are here surrounded by various encasing tubes of glass, so that the respective anode and cathode spaces communicate only through small holes with the main mass of electrolyte which acts as an intermediate space. If one observes in such a trough, which is filled for instance with fused chloride of lead, the polarization discharge by means of a galvanometer of high resistance (galvanometric voltmeter) after

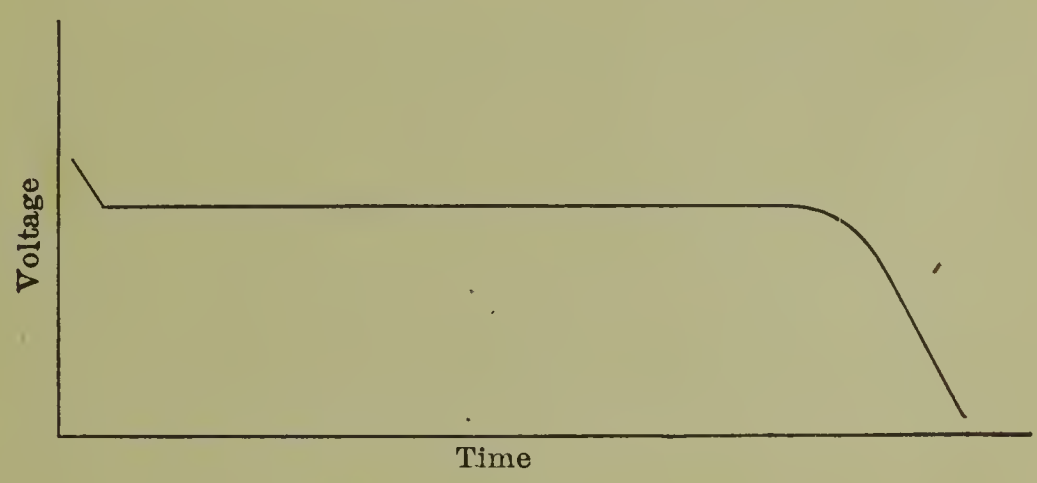


FIG. 3.— POLARIZATION CURVE.

the electrolysis has proceeded for some time, the curve thus obtained will have the form of a discharge curve of an accumulator.

There will be observed in the galvanometer a long continuing, constant deflection of about 1.2 volts at about 600 deg. C. which then gradually diminish when the electrodes become poor in polarizing material. If the anode branch of the tube is kept completely filled with chlorine gas and is protected from the atmosphere, such a deflection may, under circumstances, last for hours. When the system has been in a complete state of repose for so long a time, it can happen that a cloud (Schliere) of metallic mist flows out of the hole in the encasing around the cathode. This cloud then spreads out gradually into the middle space of the electrolyte and in spreading out in various directions it also extends to the hole in the case around the anode. But from the anodic hole a more or less thick cloud then by chance flows down into the anode space.

All these processes have up to this point no effect on the steady and completely stable position of the galvanometer needle. But at the moment when the cloud of metallic mist in its wanderings arrives at the carbon rod anode, and touches it, the deflection of the galvanometer will fall suddenly almost 0.6 to 0.8 volt, and the needle will swing to and fro with irregularity. Simultaneously the cloud in the anode space will be seen to become pale; it becomes consumed under the influence of the contact action of the pole by the chlorine present there, that is, it is changed into chloride of lead. In order now to prevent a further crowding of the metallic mist into the anode space one could cut off the cloud up at the cathode hole by slightly turning the encasing tube, so that the hole is placed in a clear part of the electrolyte which is free from the mist. The turning of the encasing tube has no effect on the galvanometer deflection, but the mist which is there then becomes completely clear due to the excess of chlorine in the anode space, and the electrolyte again becomes as before, honey-yellow and clear. As soon as this point is reached *the deflection in the galvanometer again rises to its original value of* 1.2 *volts,* and remains there as usual until the system is completely discharged. There is found in such a case the following discharge curve (Fig. 4):

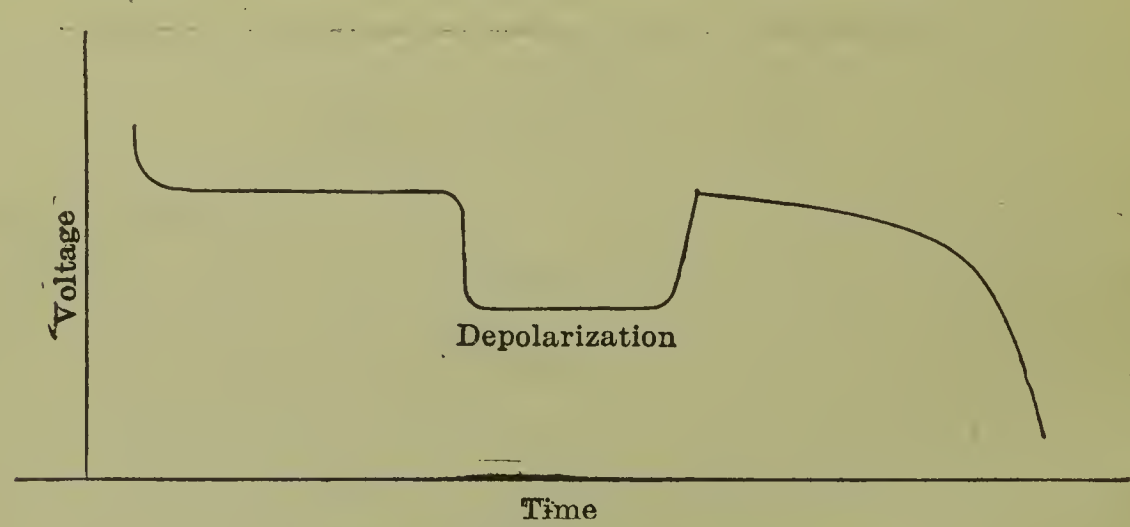


FIG. 4.— POLARIZATION CURVE.

It follows from this that one must proceed with care in the selection of the conditions of the experiment in making such polarization discharge curves. As Czepinski has shown, one no doubt obtains polarization values in the usual V-tube, but they will be too low on account of the depolarizing action of the metallic mist at the anode. In fact O. H. Weber could prove the connection between the resulting formula and the apparatus used, in which the more or

less strong depolarization is a result of the above-described phenomenon. He obtained in this way the following interesting curve sheet (Fig. 5), in which he plotted the constant discharge point as a function of the temperature.

In this the curve 1 represents the polarization for chloride of lead at different temperatures, as measured in the following apparatus. At the bottom of a wide porcelain tube, which contains the fused bath, there was a *large* amount of lead regulus, into which dipped a carbon rod well insulated from the rest of the bath by means of a porcelain tube. The anode, also a carbon rod, was in a straight tube open at the bottom,

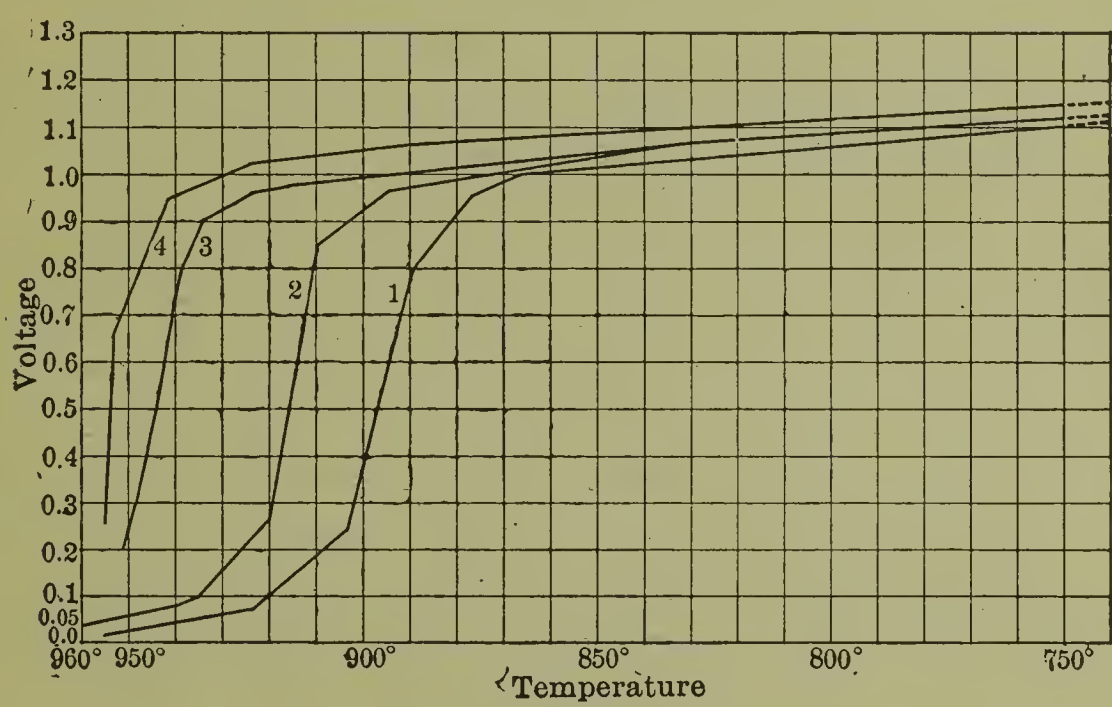


FIG. 5.— POLARIZATION CURVES.

which dipped into the bath from above and ended not far above the lead regulus. If the anode be now moved away from the regulus, and inclosed more completely by its porcelain tube, curve 2 will be obtained for the polarization values. The anode was furthermore put into a V-shaped tube which had a short and a long branch. The short branch was dipped into the fused bath. By this a marked separation of the anode space is accomplished, and curve 3 is obtained. If, finally, the lead regulus is also placed into such a V-shaped tube, whereby a complete separation of the anode and cathode spaces is accomplished, curve 4 will be obtained. Each one of the successive curves indicates higher polarization values and a smaller temperature coefficient

of polarization than the preceding one; this is true as well in the range of lower temperatures in which the eddy motions are limited (but in that case with smaller variations), as also at high temperatures at which the eddy motions are still active even with a better separation of anode and cathode, and in this case with very strong variations. Just as with the encasing the current efficiency also approaches more and more to that required by Faraday's law as was shown above, so will the normal polarization be reached thereby when Faraday's law is fulfilled, and, therefore, it may be said: *The polarization phenomena in the electrolysis of fused salts are analogous to the current efficiency phenomena.*

The best determinations of the polarization at different temperatures which were obtained in the most appropriate apparatus refer to the electrolysis of chloride of lead, chloride of zinc, and chloride of silver. The chloride of lead chain can be represented by the formula $E^t = 1.2818 - 0.000584$ ($t = 506$ deg.) according to O. H. Weber (*Zeit. Anorg. Chem.*, Vol. 21, p. 305, 1899). Furthermore, the chloride of zinc chain by: $E_t = 1.662 - 0.000751$ ($t = 430$ deg.) according to R. Suchy (*Zeit. Anorg. Chem.*, Vol. 27, p. 152, 1901). These formulas become possible because the temperature coefficient for these two combinations are constant over a long range of temperatures, which for the chloride of lead chain are between 506 deg. and 890 deg., and for the chloride of zinc chain between 430 deg. and 660 deg. For the chloride of silver chain the temperature coefficient at a low temperature is not constant; it becomes so only at higher temperatures. The Gibbs-Helmholtz formula $U = 2.23041\ (E - T\frac{dE}{dT})$ can be applied to these polarization values, which enables us to connect the combination heat of the current producing processes with the free heat of formation.

In the following tables E are the e.m.f.s of the chains, $\frac{dE}{dT}$ are the temperature coefficients, U are the values of the total energy, A is the external energy, $U - A$ the changes in the total energy comparable with the heats of combination calculated from thermochemical data which are given in the next to the last column; the last column contains the differences U (electric) $-U$ (thermic).

(C) Pb | $PbCl_2$ | Cl_2[C].

t	E	$-\frac{dE}{dT}$	U	A'	$U-A'=U_{el.}$	$U_{therm.}$	Δ
956	0.2784						
		0.1298					
955	0.4082						
		0.1231					
953	0.6545						
		0.0291					
947	0.8293						
		0.0183					
942	0.9209						
		0.0119					
937	0.9806						
		0.00246					
927	1.0052						
		0.00245					
917	1.0297						
		0.00114					
890	1.0604	.....	80.164	2.326	77.838	Constant $= U_{18°} + S_{Pb} - S_{PbCl_2} = 82.770 + 1.161 - 5.806 = 78.1555$ Cal.	—0.317
857	1.0812		80.232	2.260	77.972		—0.183
837	1.0938		80.275	2.220	78.055		—0.100
817	1.1058	Average of the temperature coefficients from 506—890° $\frac{dE}{dT} = -0.000584$.	80.294	2.180	78.114		—0.041
767	1.1320		80.155	2.080	78.075		—0.080
747	1.1427		80.109	2.040	78.069		—0.086
727	1.1536		80.072	2.000	78.072		—0.083
707	1.1641		80.017	1.960	78.057		—0.098
667	1.1830		79.809	1.880	77.929		—0.226
657	1.1878		79.763	1.860	77.903		—0.252
637	1.2008		79.823	1.820	78.003		—0.152
617	1.2173		80.048	1.780	78.268		+0.113
607	1.2233		80.054	1.760	78.294		+0.139
577	1.2398		80.008	1.700	78.308		+0.153
572	1.2428		80.012	1.690	78.322		+0.167
562	1.2488		80.017	1.670	78.347		+0.192
547	1.2557		79.933	1.640	78.293		+0.138
537	1.2612		79.915	1.620	78.295		+0.140
527	1.2668		79.906	1.600	78.306		+0.151
506	1.2818		80.030	1.558	78.472		+0.317
...	.....	0.0007404	.....	.....	.....	.....	.....
502	1.2847		85.629	1.550	84.079	83.931	+0.148

Temp.	U	A	$U-A-U_{el.}$	U_1 therm.	U_2 therm.
450°	100.93 Cal.	1.45	99.48 Cal.	$97.59-S$	$99.03-S$
500°		1.55	99.38 "	$97.46-S$	
550°		1.65	99.28 "	$97.39-S$	
600°		1.75	99.18 "	$97.27-S$	
650°		1.85	99.08 "	$97.16-S$	

Ag | AgCl | Cl_2 (Carbon).

Temp.	E.M.F.	$\frac{dE}{dT}$	U (Cal.)	$A=\frac{RT}{2}$	$U-A$	$U_{\text{therm.}}$	Δ
480°	0.902		24.00	0.75	23.25	28.14 — S	—(4.90—S)
		0.0002					
490°	0.900		23.98	0.76	23.22		
		0.0002					
500°	0.898		24.21	0.77	23.44	28.11 — S	—(4.67—S)
		0.0002					
510°	0.896		24.23	0.78	23.45		
		0.0002					
520°	0.894		24.64	0.79	23.85		
		0.0002					
530°	0.892		25.61	0.80	24.81		
		0.0002					
540°	0.890		25.61	0.81	24.80		
		0.0003					
550°	0.887		25.61	0.82	24.78	28.00 — S	—(3.22—S)
		0.0003					
560°	0.884		25.55	0.83	24.72		
		0.0003					
570°	0.881		25.90	0.84	25.06		
		0.0002					
580°	0.879		26.33	0.85	25.48		
		0.0004					
590°	0.875		26.69	0.86	25.83		
		0.0003					
600°	0.872		27.10	0.87	26.23	27.93 — S	—(1.70—S)
		0.0003					
610°	0.869		27.72	0.88	26.84		
		0.0004					
620°	0.865		28.61	0.89	27.72		
		0.0004					
630°	0.861		29.70	0.90	28.80		
		0.0005					
640°	0.856		28.70	0.91	27.79		
		0.0004					
650°	0.852		29.72	0.92	28.80	27.84 — S	—(0.96—S)
		0.0006					
660°	0.846		29.70	0.93	28.77		
		0.0004					
670°	0.842						
	Average error ±0.001						

For the two first-named chains it is an unusually remarkable fact that the temperature coefficient is constant over a long range of temperature. The author has endeavored to account for the meaning of this fact by means of a thermodynamic calculation. If the equation $A-U=T\frac{dA}{dT}$ is differentiated for T, it gives $\frac{dA}{dT}-\frac{dU}{dT}=\frac{d(T\frac{dA}{dT}}{dT}$. This gives $-\frac{dU}{dT}=T\frac{d^2A}{dT^2}$. If now $\frac{dA}{dT}$ is constant, then $\frac{d^2A}{dT^2}=0$, and, therefore, $-\frac{dU}{dT}=0$, hence $U=$ constant. As long as the temperature coefficient does not change with the temperature, the heat of combination of the reaction is

constant. But the general thermodynamic formula for the action of the total energy, according to which we recalculate these for different temperatures, is as follows:

$$U_t = U_{to} + S_1 + S_2 + \ldots + m_1 \int_{to}^{t} c_1\, dt + m_2 \int_{to}^{t} c_2\, dt + \ldots$$
$$- S'_1 - S'_2 - \ldots - m'_1 \int_{to}^{t} c'_1\, dt - m'_2 \int_{to}^{t} c'_1\, dt \ldots$$

In this equation:

m_1, m_2, m_3, represent the molecular or atomic weights of the reacting components;

m'_1, m'_2, m'_3, the molecular or atomic weights of the products of the reaction;

c_1, c_2, c_3, the specific heats of the reacting components;

c'_1, c'_2, c'_3, the specific heats of the products of the reaction;

S_1, S_2, S_3, the sums of the molecular fusion and vaporization heats of the reacting components;

S'_1, S'_2, S'_3, the sums of the molecular fusion and vaporization heats of the products of the reaction;

U the heat of combination at the temperature t, and U_{to} that at the temperature t_0.

From this it follows that U_t is constant when

$$m_1 \int_{to}^{t} c_1\, dt + m_2 \int_{to}^{t} c_2\, dt + \ldots\ldots m'_1 \int_{to}^{t} c'_1\, dt - m'_2 \int_{to}^{t} c'_1\, dt$$

equals zero or a constant. In every case it follows from this equation by differentiation:

$$m_1 c_1 + m_2 c_2 + \ldots\ldots - m'_1 c'_1 - m'_2 c'_2 - \ldots\ldots = 0.$$

For a binary compound, therefore

$$m_1 c_1 + m_2 c_2 - mc = 0$$

that is, the molecular heat of the product produced is equal to the sum of the atomic heats of the reacting components. But U might also have a value which is not absolutely constant but only approximately so, and we may write:

$$m_1 \int_{to}^{t} c_1\, dt + m_2 \int_{to}^{t} c_2\, dt - m \int_{to}^{t} c\, dt = E\varphi\,(t).$$

In this expression E is a small quantity. It shows that there is only a small dependence on the temperature. It then follows after differentiating that

$$m_1c_1+m_2c_2-mc=E_{\varphi'}(t)$$

and the latter expression is also very small whereby a law similar to the one above given follows again. If it be remembered, moreover, that the following reaction always exists

$$m_1+m_2=m$$

it follows that

$$m_1c_1+m_2c_2=(m_1+m_2)c$$

or that the specific heat of the product produced is

$$c=\frac{m_1c_1+m_2c_2}{m_1+m_2}.$$

The so-called thermochemical rule of mixtures, therefore, also applies, with a very close approximation, to the specific heat for the systems which were investigated.

In the adjoining tables for chloride of lead and chloride of zinc a small, but nevertheless very definite, range in the variations of the calculated values of the heat of combination from those observed indicates that the regularity here found is not an absolute sharply defined one. The change in the specific heat of the reacting components, lead and chlorine, is rather greater than that of the material produced, lead chloride. Nevertheless, the slight bend which the curve of the e.m.f's shows toward the temperature is so small that it is preferable to assume the regularity here shown and to place the algebraic sum of the specific heats involved equal to zero, when one calculates the action of the total energy from the heats of combination.

In closing this section attention is called in a few words to the fact that in the polarization of fused salts a time phenomenon also develops. If the polarization discharge is observed in the electrolysis of a fused salt, for instance, lead chloride, in an electrolytic trough in which the anode and cathode spaces are not separated from each other by a great distance, the galvanometer indicates for the discharges only an extremely short normal dis-

charge point. If the polarization (measurements?) be now repeated continually, the discharges being observed repeatedly during the test, the constant discharge point will become longer and longer, until finally there will result a nearly normal discharge curve having the appearance of the one drawn above. This phenomenon, observed by Sacher (*Zeit. Anorg. Chem.*, Vol. 28, p. 385, 1901), and by Auerbach (*Zeit. Anorg. Chem.*, Vol. 28, p. 1, 1901), is again completely analogous to the relations of the current efficiencies at the anode, and indicates here, as it does there, the degree of saturation of the carbon rod with chlorine. When the carbon rod still continues to absorb chlorine, the capacity of the electrode is small and the discharge point short. When it is saturated the discharge curve becomes normal and Faraday's law is fulfilled at the anode, as has already been shown above.

The researches of the author with J. F. Sacher have brought out very interesting polarization discharge curves for fused sodium hydrate. It was found that there was a double fall in these discharge curves (like that which has lately been shown frequently for various accumulators in which the plates are not of lead). One of the constant discharge points was at 2.14 to 2.18 volts, the other at 1.3 to 1.1 volts; this corresponds to the charging of the cathode on the one hand with metallic sodium, on the other with hydrogen, opposite to an anode which is charged with oxygen. It was interesting to verify these polarizations in the reverse way by plotting the curve of decomposition voltages. The author, together with Sacher, carried this out for iron as well as for platinum chlorides, whereby they studied and recorded the required preparation of the iron electrode for this purpose (passive state of the iron). The plotting of the curve of decomposition voltage showed that the point of the discharge of hydrogen disappeared when the fused bath is completely free from water, so that the pure sodium hydrate is electrolytically decomposed entirely into sodium at the cathode and into oxygen (discharge of OH ions) at the anode.

The decomposition curves were taken at two electrodes of the same size, as well as at a large anode and a small cathode, and at a large cathode and a small anode. Iron and platinum electrodes were used. The results obtained for the decomposition voltage agree completely with the polarization values so that the meaning of the decomposition point is thereby made completely

clear. In the following table the results of the researches are collated:

Method.	1st point.	2d point.
Polarization discharge	1.3—1.1	2.14—2.18
Two equal electrodes	(1.1)	2.23—2.25
Large anode, small cathode	1.15—1.16	2.06—2.09
Large cathode, small anode	1.33—1.31	

The proof that hereby water was formed at the anode was subsequently supplemented to the work of Lorenz and Sacher by Le Blanc and J. Brode (*Zeit. f. Elektrochemie,* Vol. 8, p. 717, 1902).

The effect which the formation of metallic mist has on the deposition of the alkaline metals is expressed in the work of R. Lorenz and W. Clark (*Zeit. f. Elektrochemie,* Vol. 9, p. 269, 1903). They succeeded in depositing potassium from fused potassium hydrate by encasing the cathode.

In concluding this review of our knowledge to the present date in the sphere of the theory of the electrolysis of fused salts, the author desires to express the wish that the industries may make advantageous use and draw useful conclusions from it.

Especially in the United States of America extended use is made of the electrolysis of fused salts. Besides the larger processes, like the aluminum process which has been in operation a long while, many experiments are also made to apply the electrolysis of fused salts to new industrial applications. Perhaps some one or other of the features explained above may prove to be of use in practice.

There being no discussion on the paper, the Chairman requested Dr. Bancroft to present Prof. Dr. W. Ostwald's paper, in the absence of the author.

ELECTROLYSIS AND CATALYSIS.

BY PROF. DR. W. OSTWALD, *University of Leipzig.*

The chemical result of the conduction of an electric current through an electrolyte is made up of two very different effects, namely the phenomena of the *conduction* through the electrolyte and those concerned with the *transfer of electric charges* at the electrodes. With respect to the first effect, we have clear and definite conceptions, based on the universally confirmed theory of Hittorf. According to this theory, the mechanism is of the greatest simplicity, namely, the cations and anions migrate in opposite directions and with mobilities which depend mainly on the specific nature of the ions, but also on the solvent, the concentration and the temperature. The process which results in the second effect — namely the ionic discharge or the general transfer of charges at the electrodes — also seemed at first to be simple and clear. But the assumption that the ions which accomplish the transportation of the current through the electrolyte are also the materials which undergo the electric change at the electrodes, could not be supported; it was the recognition of the very fact that both can be different, which made possible the development of the proper explanation of the phenomenon of electrolytic conduction itself. Berzelius still based his electrochemical system on such an incorrect conception of the electrolytic phenomena. He at first and chiefly tested the salts of the alkaline metals and earths; since *bases* and *acids,* besides hydrogen and oxygen, result from their electrolysis, he regarded the former two substances as the real constituents of the salts, and based his entire chemical system on this misconception derived from his experiments. Even Faraday held rather erroneous views in this regard, though we owe to him the name and conception of the ions. The first one who was consistent was *Daniell,* who throughout assumed the metals to be the cations of the salts. This scientist's conception of the mechanism of the transportation of electricity by the ions was still imperfect, and it was Hittorf who then worked out the theory in this respect and reduced it to a perfectly simple and clear one; to him we owe

the statement that electrolytes are salts, and the experimental methods for determining the nature of the ions in every given case, as also the ratio of their migration velocities independently of any possible electrode reactions.

The new idea of decisive importance was that of a *secondary reaction.* While by the conduction of the current through the electrolyte a certain ion may be transferred to the cathode, it does not necessarily follow that it is deposited or liberated there. In a solution of potassium chloride it is undoubtedly the potassium ion which transports the positive electricity to the cathode. Yet it does not appear there as the product of electrolysis, but in its stead, potassium hydroxide and hydrogen are formed. This is explained by the conception that directly or primarily potassium is deposited, which, however, cannot exist in contact with the water of the solution and reacts with it, forming potassium hydroxide and hydrogen.

First of all, this view enables us to conceive the same simple mechanism for the conduction of the current through an electrolyte, in the two theoretically fully analogous cases of the electrolysis of the salts of heavy metals which do not decompose water, and the electrolysis of the salts of light metals which decompose water, although both cases are apparently quite different from an experimental point of view. Another result is that the apparent contradiction to Faraday's law is avoided which, in the case of electrolysis of salts of light metals, could be found in the fact that, besides the liberation of oxygen and hydrogen, the formation of acid and alkali appear as immediate effects of the electrolysis. Finally our view gives an explanation of the fact that in some cases, instead of the secondary reactions, it is possible to get the primary products by means of a slight modification of the conditions of the experiment. For instance, in the case of the alkali metals this is possible by the use of a mercury cathode.

In the course of time the necessity has manifested itself to consider a great many reactions as secondary. The best known example is the decomposition of water between inert electrodes. Since water itself is a poor conductor, alkali or acid is added, and in former descriptions of this method it was stated that these additions are made only for the purpose of rendering the water a "better conductor." Now we know with sufficient certainty that the conduction of the current is really accomplished by the ions of the additions, and, in the case of an acid, we consider the oxygen

developed at the anode as the result of a secondary reaction between the discharged anion and the solvent water, while in the case of an alkali, we must assume secondary reactions even at both electrodes, namely at the cathode the reaction between alkali metal and water and at the anode the change of the discharged hydroxyl ions into oxygen and water.

By the development of modern electrochemistry our views on these questions have been modified so as to be more precise. If at an electrode several processes are possible by means of which the transfer of electricity from the electrolyte into the electrode may take place, we have to assume that that reaction will take place for which the potential difference is a minimum. Or in other words, if we gradually increase the e.m.f. applied at the terminals of the cell, beginning with zero e.m.f., then, of all possible ionic discharges, those will first occur which require the smallest potential difference.

However, the potential difference for any electrode reaction has in general no constant value, but depends upon the temperature and to a considerable degree upon the *concentration;* the range of the strongest influence is exclusively at *low* concentrations. If we start from "molar" solutions and increase the concentration, we cannot go beyond 10 times molar concentrations for experimental reasons, because more concentrated solutions of electrolytes cannot in general be prepared. Within the limits mentioned, the maximum possible difference is about 0.06 volt for the electrolytic production of any constituent of these solutions out of the concentrated or out of the dilute solution. On the other hand, if we start again with molar solutions and decrease the concentration, the same difference of e.m.f. (0.6 volt) is found for every decrease of the concentration to one-tenth its former value; hence for 0.001 molar solutions compared with molar ones, it has already increased to 0.17 as a maximum, and for 0.000001 molar solutions it is twice as great. For infinitely dilute solutions it is theoretically infinite, but experimentally one does not exceed two volts.

The following important conclusion may be drawn herefrom. If there are several possibilities for the reaction at one electrode, the chemical reaction which really occurs depends not only upon the nature of the possible chemical reactions, but also upon the concentration of the substances which are present, and by suitably varying the latter we can bring any reaction to any point in the voltage series.

Now it is a universal fact that the electrolytic process itself results in a decrease of the concentration of that substance in the neighborhood of the electrode which is involved at that moment in the electrode reaction. Hence any such reaction has the tendency to stop by itself and to be replaced by that reaction which can and will take place as the next one with increasing voltage. Moreover, since the voltage is influenced only by the concentration *at the electrode itself,* not by the average concentration in the whole electrolyte, this "polarization" would necessarily take place almost instantaneously after the current has begun to flow, if there were not other processes which bring the exhausted kind of ion again in sufficient quantity to the electrode.

These compensating influences are of a twofold kind. First, we have diffusion which tends to make good any decrease of concentration with a force proportional to the existing concentration difference. Secondly, we may have chemical reactions which are caused by the exhaustion of the electrolytically changed ions, since the equilibrium which had been disturbed by their disappearance begins to reconstitute itself and, therefore, also tends to counteract the loss. Both compensating processes, however, start only after the loss had been established, and are, therefore, never able to reproduce the original condition. The result is always a polarization, i. e., an e.m.f. which counteracts the applied e.m.f.[1]

The value of the e.m.f. of polarization evidently depends upon the final decrease of concentration of the electrolytically changed ion. For this purpose we have to consider the stationary condition which is reached after the first variable processes have terminated. For the case in which the compensation for the exhausted ions is accomplished by diffusion only. Helmholtz has already given the underlying principles of the reaction. These may be briefly summarized as follows:

The current causes a consumption of the active ion at the electrode surface, the quantity consumed being proportional to the quantity of electricity which has passed. But the electrolytic migration of the ions does not bring as many new ions to the cathode as are consumed; it brings only a certain portion of this number, this portion being given by the ratio of the migration velocity of the active ion to the sum of the migration velocities of

1. There are known a few cases of abnormal polarization in which the current causes an e.m.f. of polarization of the same direction as the applied e.m.f.: their theoretical explanation is possible on the basis of the theory given in what follows.

both ions. Hence there must necessarily result ionic exhaustion which is counteracted by diffusion. The exhaustion progresses so far until diffusion — which simultaneously increases on account of the increasing concentration difference — brings back to the electrode exactly the missing amount of ions in the form of its salt. There will, therefore, be produced finally a certain distinct concentration difference between the electrode surface and the main part of the solution, and there will be a corresponding distinct e.m.f. of polarization. Since the diffusing quantity of salt is proportional to the coefficient of diffusion and to the *difference* of concentration, while the e.m.f. of polarization is proportional to the *ratio* of the concentrations, it follows that with the same current density the e.m.f. of polarization must become the greater the lower the total concentration of the active ion.

These considerations hold good directly for primary electrolysis in which the current is transported by the same ion which undergoes the change of concentration at the electrode. For secondary electrolysis we have only to consider what the influence of the current will be, according to Faraday's law, upon the concentration of the electrolytic ion at the electrode. Let us consider, for instance, the case of "water decomposition," and let us distinguish the two cases in which, for increasing the conductivity, an acid or a base is added. With an acid solution we have to consider at the cathode the concentration of the hydrogen ion and we then have primary electrolysis. At the anode we had to consider first the concentration of the anion, for instance the SO_4 ion. By its reaction with water, oxygen and sulphuric acid is formed according to the equation

$$SO_4'' + H_2O = H_2SO_4 + O,$$

i. e., this process yields sulphuric acid which disintegrates again into its ions. The concentration of the SO_4 ion is, therefore, not diminished but increased, and this increase corresponds exactly to the decrease of the concentration at the cathode. Diffusion will now carry away the sulphuric acid from the anode and this will lead to a stationary condition. The total result is not a compensation of the two e.m.f's. of polarization at the electrodes, but since an *increase* of concentration has a smaller influence on the potential than an equal *decrease*, we will ultimately have a polarization in the ordinary sense, i. e., the passage of the current is rendered

more difficult, and this will be the case to a greater extent the higher the current density and the smaller the total concentration.

If a caustic potash solution is electrolysed, we have a similar increase of the potassium hydroxide concentration at the cathode, due to the ionic migration, since it is not removed there from the solution, and we thus have here quite similar conditions as exist for sulphuric acid near the anode. At the anode we have, in the case of caustic potash electrolysis, the reaction $2OH' = H_2O + O$. The concentration of HO is approximately proportional to that of the potassium, but the latter decreases on account of the migration of the ions. Furthermore, immediately at the anode a layer of pure water is formed. The total result in this case is again a polarization in the ordinary sense.

All these considerations are based, however, upon the further supposition that *the chemical reactions by which the secondary products are formed occur with a speed which is infinitely great in comparison with the other processes.* This is a supposition which, while very approximately fulfilled in the cases which we have considered, yet is not necessarily fulfilled in all cases. If we have to do with reaction velocities which are not infinitely great, there arise a great many new questions which we had no need of answering so far.

It may be asked, for instance, whether at the anode in a potassium hydroxide solution, the secondary reaction $2OH = H_2O + O$, or even $4OH = 2H_2O + O_2$ occurs, or whether we do not have a primary reaction, namely the discharge of bivalent oxygen ions. True, the existence of such an ion O'' has not yet been proved; it can never exist in considerable quantities, because it soon reacts with water according to the equation

$$O'' + H_2O = 2OH'$$

and forms hydroxyl ions. On the other hand, one may state that it must always be present in very small quantities wherever hydroxyl ions are present, since the above reaction also takes place in the reverse direction, as read from the right to the left hand of the equation, and the simultaneous concentrations of the two kinds of ions are determined by the (unknown) equilibrium constant of this reversible reaction. As long as this reaction also takes places with a speed which is infinitely large compared with that of the electrolytic processes, it does not matter which reaction is assumed, since no measurable quantity is thereby influenced; it is, therefore, not possible to decide which of the different possible

reactions really occurs and a discussion of this point does not fulfill any useful purpose.

Let us now imagine the possibility of rendering the reaction between hydroxyl ions and bivalent oxygen ions infinitely slow by some means. It would then be possible to decide which of the two reactions occurs at the electrode (under the supposition that it is either the one or the other). If it is the hydroxyl ion which is discharged, the decrease of concentration, produced by a given current, will have a relatively much smaller effect than an equivalent decrease of concentration of the oxygen ion which is present in a much smaller concentration. Under equal conditions we would, therefore, get a small polarization in the first case and a very strong polarization in the second case; and by measurements of the polarization we could decide which of the two reactions really takes place.

Such means of changing the speed of a given reaction within very wide limits really exist in chemistry in what is called *catalyzers.* From this it is at once evident what a very essential and important part the catalyzers are able to play in electrolytic action. By retarding one of the possible reactions by means of a negative or retarding catalyzer, we are able to *exclude* its influence from the electrolytic process. By accelerating by means of a catalyzer a reaction which is of itself slow, we can *include* it in the electrolytic process. In other words, we are no longer compelled to let the current act in the way stated by the above simple law, but, in principle, we are now able, *by applying suitable catalyzers, to prescribe to the current that reaction which we want to have to take place,* and it does not matter at which point of the voltage series this reaction is situated.

This fundamental idea may be applied in two directions. First in *synthetic* work; if we suppress by negative catalyzers those reactions which would take place before the desired one, we can bring the desired reaction to the front; or if the reactions which take place before the desired one occur with a low speed, we can accelerate the speed of the desired reaction by means of a positive catalyzer and can thus produce the same effect. The second application is *for analyzing the reactions which really take place at the electrodes.* If these reactions are essentially influenced by a certain addition, and if we know the single reaction which is altered catalytically by the addition, we can conclude that this reaction takes an essential part in the electrode process. If a catalyzer of known

specific activity does not influence the electrode reactions, we can draw the reverse conclusion and state that that reaction is not a part of the electrode process.

In connection with this, it should be emphasized that what is called above briefly *the electrode process* is in reality a rather complex phenomenon. In the simplest case — for instance, in the primary electrolysis of a silver salt — this reaction consists in the change of the silver ion to metallic silver. But "metallic silver" is not a well-defined substance, since we know elementary silver in very different allotropic states. Here the very general rule manifests itself that a system, when changing from one state to another one, first assumes the unstable intermediate states which change step by step into the more stable ones; in the case of explosive antimony, detected by Gore, it is well known that one of these states remains metastable for a longer time. One may say, therefore, that the first product in the cathodic deposition of silver is that which is formed as the next step from the silver ion after the loss of its positive charge, i. e., silver dissolved in water, probably of the molecular weight of Ag. On account of the presence of white metallic silver the silver cannot continue to exist in this state, but changes into the stable form of white silver. At the cathode a distinct proportion of dissolved silver ions to dissolved silver metal will, therefore, be established, and this proportion will determine the potential by means of an equation similar to that given by Peters[2] for the potential of a mixture of ferrous and ferric salts. The greater the speed of the change of dissolved silver into the white solid metal, the smaller will be the concentration of the dissolved silver metal and the more it will approximate that which is given by the self-solubility of white silver[3] and which, therefore, represents the equilibrium potential of a silver electrode.

Similar considerations hold good for the secondary reactions at an electrode. Thus, as the primary anodic product of the electrolysis of dilute sulphuric acid, a substance SO_4 may be assumed which reacts with the solvent water with any (probably very high) speed, to form oxygen and sulphuric acid. In the case of concentrated sulphuric acid which contains mainly the ion $H'SO'_4$, it is not the substance HSO_4, but its polymerisation product $H_2S_2O_8$

2. *Zeit. f. Phys. Chemie*, v. *26*, p. 200, 1898.

3. Such a solubility must be assumed in any case. This follows from general reasons and from the facts, detected by Naegeli, of the accumulating poisonous action, the "oligodynamics" of water in contact with metallic silver.

which is obtained, or its ions, as the conceivable primary product. If, however, the anode has too strong catalytic properties, for instance, if it consists of a large platinum plate, the persulphuric acid which is formed soon disintegrates into sulphuric acid and oxygen, and the unstable intermediate product does not remain.

It will thus be seen that even the simplest electrode reactions are made up of a plurality of reactions following each other step by step. Since each of the same can be influenced catalytically, it is already evident that a very great variety of results is possible. We should furthermore consider that many of the unstable substances which are formed as intermediate products during electrolysis, and which quickly disappear, are not yet known separately with respect to their properties, and especially with respect to the action of catalyzers upon the same. Under these circumstances it will be evident what an abundance of peculiar and unexpected phenomena we may hope to detect in this way, and how much new knowledge we may expect to obtain from a systematic investigation of this field. The literature of electrochemistry already contains a great number of separate facts which are not only understood more easily but applied with greater safety, if considered from the points of view given in this paper (a large portion of which was suggested by other scientists, since, about six years ago, I emphasized the necessity of taking into consideration catalytic action in the investigation of the phenomena of electrolysis). I regret that I cannot go into details; I wish to remark only that for some time Prof. Luther with his scholars has attacked this problem from different sides; the papers already published by them, and still more the unpublished investigations, will show the generalty and variety with which this scientist has understood developing this principle and rendering it useful.

The CHAIRMAN: If there are no remarks upon this paper of Dr. Ostwald, it will be published in full in the *Transactions*.

I should like to take this occasion to congratulate the Section on the attendance and the character of papers we have had for the last three days, and to say that we have now concluded the list of papers assigned to Section C of the International Electrical Congress.

There being no further business before the Section, the Chairman declared it adjourned.

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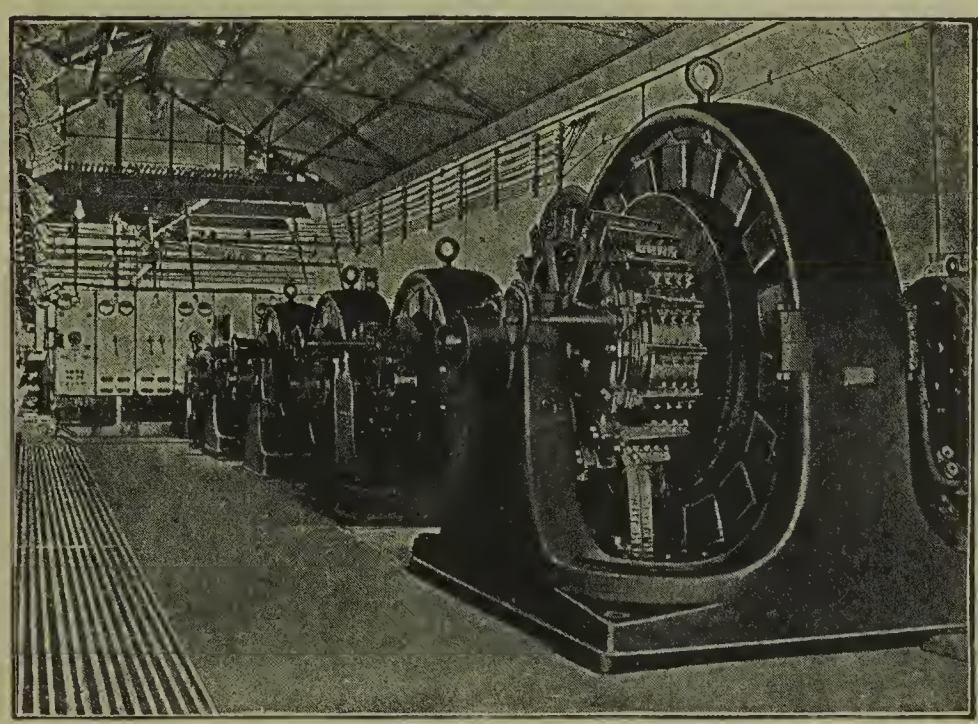

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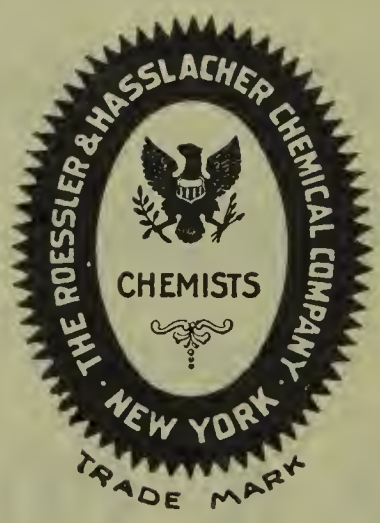

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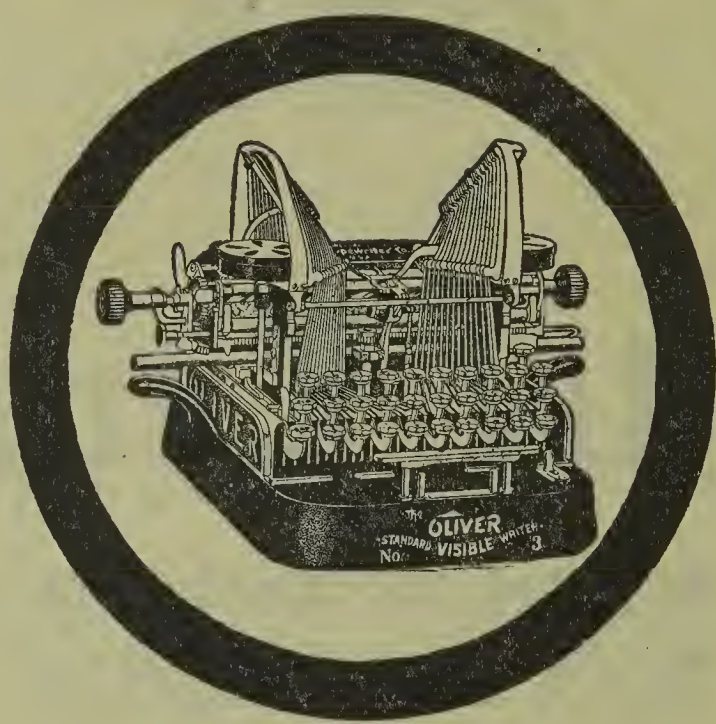

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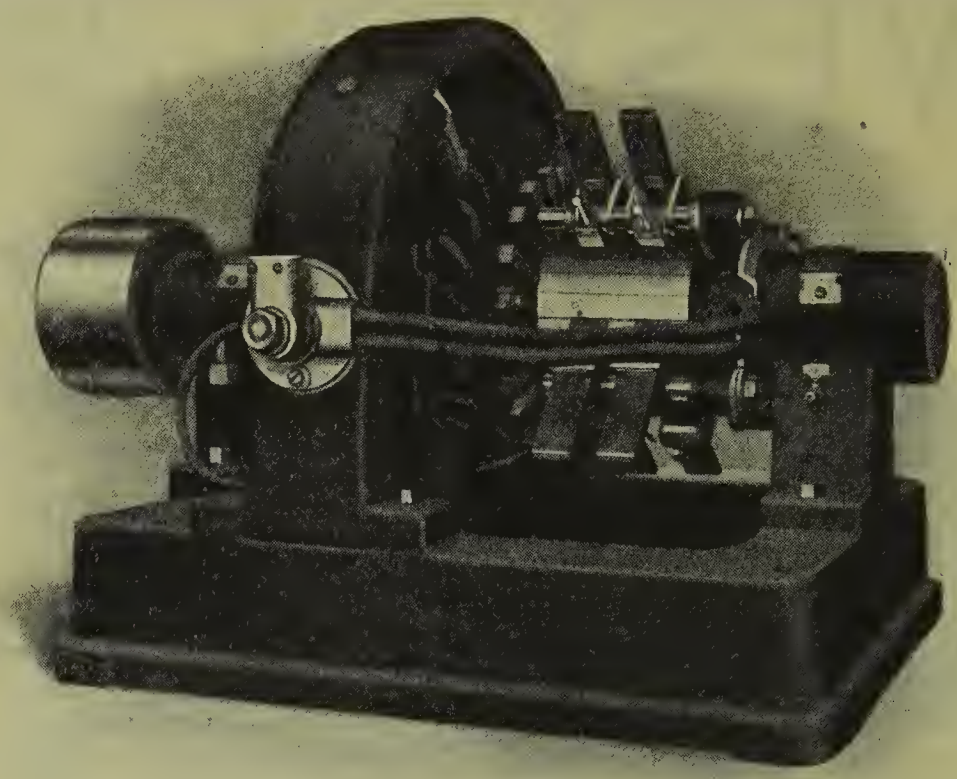

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